

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application of: Roy Lee Hood, et al	:	Examiner: Elizabeth M. Cole
	:	
Serial No.: 10/814,679	:	Group Art Unit: 1771
	:	
Filed: March 31, 2004	:	Attorney Docket No.: 713629.417
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For: MULTI-COLOR MATS AND APPARATUS	:	Customer No.: 027128
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**APPEAL BRIEF TO BOARD OF PATENT
APPEALS AND INTERFERENCES UNDER 37 C.F.R. § 41.37**

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Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

———— Appellants submit the following Appeal Brief to the Board of Patent Appeals and
Interferences in response to a new final Rejection, dated October 22, 2008:

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1. The Real Party In Interest

The real party in interest for the above referenced application is Solutia, Inc., a Delaware corporation, located at 575 Maryville Center Drive, St. Louis, Missouri 63141, United States of America, the Assignee of record of the entire right, title and interest in the invention and the patent application.

2. Related Appeals and Interferences

There are no other appeals or interferences known to Applicants, (Appellants), the Applicants' (Appellants') Legal Representative or Assignee which will directly affect, or be directly affected by, or having a bearing on, the Board of Patent Appeals and Interferences' decision in the pending Appeal.

3. Status of Claim

Claims 1-5, 7-15 and 34-47 are currently pending in the application. Claim 6 has been cancelled. Claims 16-33 have been withdrawn.

Claims 1-5, 7-15, and 34-47 stand rejected and are the subject of this appeal. Claims 1, 34 and 47 are the only independent claims.

Applicants reserve their right to file additional applications to continue the prosecution of all withdrawn or cancelled claims.

4. Status of Amendments

In the current application, an initial Rejection was mailed on January 27, 2005. On April 27, 2005, Applicants submitted an Amendment in response to the Rejection. A First Final Rejection was mailed June 24, 2005. On October 21, 2005, Applicants submitted an Amendment in response to the Final Rejection and requested Continued Examination. A Rejection was mailed on December 21, 2005. On April 14, 2006, Applicants submitted an Amendment in response to the Rejection. A Second Final Rejection was mailed on June 16, 2006. On August 1, 2006 a telephone conference took place with the Examiner. An Early Response to the Second Final Rejection was submitted on August 2, 2006. An Advisory Action before the Filing of an Appeal Brief was issued on August 9, 2006. On September 6, 2006, Applicants submitted an Amendment in response to the Second Final Rejection and requested Continued Examination. An Office Action was mailed November 16, 2006. On March 8, 2007, Applicants submitted an Amendment in response to the Second Final Rejection. A Third Final Rejection was mailed on May 11, 2007. On July 9, 2007, Applicants submitted a Notice of Appeal. Briefs on Appeal were filed on September 10, 2007, October 18, 2007 and January 18, 2008, after which a fourth Final Rejection was issued October 22, 2008.

No further amendments were filed and all of the above referenced amendments were entered into the record.

5. Summary of the Claimed Subject Matter

The present invention is directed generally to a three dimensional polymeric article, for example, an artificial turf mat and such a product as produced by a defined process. The article has a planar base portion with a first side and a second side and at least one (Claim 1) or more (Claim 34) projecting elements having a lower portion and a terminal portion. The projecting element extends from one side of the base. Various portions of the article are made from different polymers. The base portion and the projecting element(s) are an integral molded thermoplastic structure.

Independent Claim 1. Claim 1 is directed to a three dimensional molded article (Pg. 1, L 7) having a planar base (Pg. 4, L's 5-9, Fig. 1, No. 1) with first and second sides (Pg. 1, L's 27-30). At least one projecting element is provided and has a lower part and a terminal part (Pg. 4, L's 5-14, Fig. 1, Nos. 2, 3). The projecting element portion extends from the first side of the base. The lower part of the projecting element includes a core portion and a surface portion (Pg. 6, L's 23-30, Pg. 7, L's 1-13). The core and the terminal part of the projecting element are formed of a first polymer. The surface portion is formed of a second polymer (Pg. 3, L's 7-17, Pg. 6, L's 23-30, Pg. 7, L's 1-13). The base and the projecting element are an integral molded construction (Pg. 3, L's 7-17).

Dependent Claim 2. Claim 2 further specifies that the first polymer contains a first colored pigment and the second polymer contains a second colored pigment.

Dependent Claim 3. Claim 3 further specifies that the base contains a pigment that is different from the terminal part of the projecting element.

Dependent Claim 4. Claim 4 further specifies that the projecting element is a plurality of projecting elements each having a terminal part. The base and a portion of the plurality of

terminal parts for the plurality of projecting elements contain the same pigment and a portion of the plurality of terminal parts for the plurality of projecting elements contain a different pigment than the base.

Dependent Claim 5. Claim 5 further specifies various types of polymers for the first and second polymer materials.

Dependent Claim 7. Claim 7 further specifies that the article includes material selected from the group of dyes, pigments of distinct colors and other fillers.

Dependent Claim 8. Claim 8 further specifies that the first and second polymer material is polyethylene.

Dependent Claim 9. Claim 9 further specifies that the base includes a slip resistant sheet laminated to the base.

Dependent Claim 10. Claim 10 further specifies that the base includes open spaces.

Dependent Claim 11. Claim 11 further specifies that the at least one projecting element includes a plurality of such elements and that the base contains a pigment that is different than the pigment in at least a minority of the plurality of projecting elements.

Dependent Claim 12. Claim 12 further specifies that the base contains a distinct pigment.

Dependent Claim 13. Claim 13 further specifies that the first and second polymers comprise polyethylene and a density for the polymer.

Dependent Claim 14. Claim 14 further specifies that the article includes at least one dispersed functional filler selected from minerals, alumina, metal oxides, conductive fillers and conductive polymers.

Dependent Claim 15. Claim 15 further specifies that the projecting element includes a plurality of projecting elements and that each has a terminal part and at least some of the plurality of terminal parts are formed from at least one distinct polymer.

Independent Claim 34. Claim 34 is directed to a three dimensional polymeric article (Pg. 1, L 7). The article includes a generally planar base portion (Pg. 4, L's 5-9, Fig. 1, No. 1) that has first and second sides (Pg. 4, L's 5-9, Fig. 1, No. 1). It also includes a first plurality of projecting element portions and a second plurality of projecting element portions (Pg. 1, L's 27-30, Fig. 1, Nos. 2, 3). Each of the element portions has a lower part and a terminal part and extends from the first side of the base (Pg. 4, L's 5-14, Fig. 1, Nos. 2, 3). The first plurality of projecting element portions are formed from a first polymer material and the second plurality of projecting elements are formed of a second polymer material (Pg. 3, L's 11-17, Pg. 4, L's 15-20, Pg. 6, L's 23-3, Pg. 7, L's 1-13). The base portion and the first plurality of projecting elements and the second plurality of projecting elements being an integral one piece thermoplastic article of molded construction (Pg. 3, L's 7-17).

Dependent Claim 35. Claim 35 further specifies that the first polymer material contains a pigment of the first color and the second polymer material contains a pigment of the second color.

Dependent Claim 36. Claim 36 further specifies that the base contains a pigment that is different from that of the first plurality of projecting elements.

Dependent Claim 37. Claim 37 further specifies that the base contains a pigment that is different from that of the at least one second plurality of projecting elements.

Dependent Claim 38. Claim 38 further specifies various polymers from which the first and second polymer materials are selected from.

Dependent Claim 39. Claim 39 further specifies that the article further includes material from the group consisting of dyes, pigments of distinct colors and other fillers.

Dependent Claim 40. Claim 40 further specifies that at least one of the first and second polymer materials is polyethylene.

Dependent Claim 41. Claim 41 further specifies that the article includes a slip resistant sheet laminated to the base.

Dependent Claim 42. Claim 42 further specifies that the base includes open spaces to facilitate cleaning.

Dependent Claim 43. Claim 43 further specifies that the base contains a pigment that is different than that of at least a minority of the plurality of projecting elements.

Dependent Claim 44. Claim 44 further specifies that the base contains a distinct pigment.

Dependent Claim 45. Claim 45 further specifies wherein at least one of the first and second polymer materials includes polyethylene with a specified density.

Dependent Claim 46. Claim 46 further specifies that the article include at least one disbursed functional filler selected from a group of listed fillers.

Independent Claim 47. Claim 47 is a product by process claim that produces a multi-color mat (Pg. 3, L's 7-20) with a planar base portion (Pg. 4, L's 5-9, Fig. 1, No. 1) and a plurality of projecting elements (Pg. 1, L's 27-30, Fig. 1, Nos. 2, 3) having a proximal end portion and terminal end portion (Pg. 4, L's 5-14, Fig. 1, Nos. 2, 3). The proximal end portions have a core portion of one polymer and a surface portion of a second polymer (Pg. 6, L's 23-30, Pg. 7, L's 1-13). The mat is made by molding the base and surface portions as an integral

structure and the cores and respective terminal end portions each as an integral structure that is integral with a respective proximal end portion (Pg. 3, L's 7-17).

6. Grounds of Rejection to Be Reviewed On Appeal

Claims 1-5, 7-15 and 34-47 are pending in the application and subject to this appeal. Claims 16-33 which are not part of this appeal are withdrawn from consideration. Claim 6 was cancelled. Claims 1, 34 and 47 are independent claims. The remainder of the claims are dependent claims. The claims stand variously rejected as being either anticipated or obvious over various references as detailed below. Claims 34-39, 41-44 stand rejected as anticipated under 35 USC 102(b) by Rochlis, U.S. Patent 3,312,583. Claims 1-5, 7, 9-13, 15, 47 stand rejected as being obvious under 35 USC 103(a) over Rochlis in view of Akeno, et al., U.S. Patent 5,657,517. Claims 8, 40, 45-46 stand rejected as being obvious under 35 USC 103(a) over Rochlis in view of Akeno in further view of Clune, U.S. Patent 6,162,040. The foregoing three rejections are newly presented rejections over newly applied art. Claims 1, 3, 5, 7, 8, 10-12, 34-40, 42-44 stand rejected as being anticipated under 35 USC 102(e) or in the alternative obvious under 35 USC 103(a) over Sallee, U.S. Patent 5,976,643. In this rejection, there is no specific discussion of claims 39 or 42 and there is a discussion of claim 15 which was not rejected in this specific rejection. Claims 2, 4 stand rejected as being obvious under 35 USC 103(a). Claims 13, 45 stand rejected as being obvious under 35 USC 103(a) over Sallee in view of Rawlinson, U.S. Patent 4,329,196. Claims 14, 46 stand rejected as being obvious under 35 USC 103(a) over Sallee in view of Sesselmann, U.S. Patent 5,790,987.

Solely for purposes of simplifying this appeal, Applicants concede that the patentability of dependent claims 2, 3, 5-10, 12-14, 35-46 rises or falls on the patentability of their respective independent claims.

7. The Relevant Law

Anticipation

It is axiomatic that for a reference to support an anticipation rejection, it must disclose each and every element of the claim.

Anticipation requires that every limitation of the claim be found, either expressly or inherently, in a single prior art reference device or practice. See *Apple Computer, Inc. v. Articulate Systems, Inc.*, 234 F.3d 14 (Fed. Cir. 2000); *Gelcher v. Davidson*, 116 F.3d 1454 (Fed. Cir. 1997). That is, the reference must sufficiently describe the claimed invention so as to place it in the possession of the worker of ordinary skill in the art. *In re Paulsen*, 30 F.3d 1475 (Fed. Cir. 1994). However, the law does state that a reference disclosing a product inherently possessing a claim feature is still anticipatory but only if such inherency “would be appreciated by one of ordinary skill in the art.” *Glaxo, Inc. V. Novopharm Ltd.*, 52 F.3d 1043 (Fed. Cir. 1995).

The Board of Patent Appeals in *Ex parte Skinner*, 2 U.S.P.Q. 2d 1788 (Bd. Pat. App. 1986), held that the Examiner must provide some evidence or scientific reasoning that a functional limitation is an inherent characteristic of the prior art.

The Federal Circuit addressed the issue of anticipation through inherency in *Elan Pharmaceuticals, Inc. v. Mayo Foundation For Medical, Education and Research*, 304 F.3d 1221 (Fed. Cir. 2002). The court in finding no anticipation stated:

“The single reference must describe and enable the claimed invention, including all claim limitations, with sufficient clarity and detail to establish that the subject matter already existed in the prior art and that its existence was recognized by persons of

ordinary skill in the field of the invention... The reference must describe the applicant's claimed invention sufficiently to have placed a person of ordinary skill in the field of the invention in possession of it... When anticipation is based on inherency of limitations not expressly disclosed in the assertedly anticipating reference, it must be shown that the undisclosed information was known to be present in the subject matter of the reference... An inherent limitation is one that is inherently present; invalidation based on inherency is not established by "probabilities or possibilities"... Inherency cannot be based on the knowledge of the inventor; facts asserted to be inherent in the prior art must be shown by evidence from the prior art... No doctrine of patent law is better established than that a prior art patent or other publication to be an anticipation must bear within its four corners adequate directions for the practice of the patent invalidated. If the earlier disclosure offers no more than a starting point for further experiments, if its teachings will sometimes succeed and sometimes fail, if it does not inform the art without more how to practice the new invention, it has not correspondingly enriched the store of common knowledge, and it is not an anticipation".

A patent claim "cannot be anticipated by a prior art reference if the allegedly anticipatory disclosures cited as prior art are not enabled". See, Rasmusson v. Smithkline Beecham Corporation, 413 F.3d 1318, 75 U.S.P.Q. 2d 1297 (Fed. Cir. 2005), citing to *Elan*, supra. The standard for what constitutes proper enablement of a prior art reference for purposes of anticipation under §102, however, differs from the enablement standard under §112. The *Rasmusson* court in citing to *In re Hafner*, 56 C.C.P.A. 1424, 410 F.2d 1403 (C.C.P.A. 1969), a case involving a unique fact situation where an inventor was trying to claim filing date priority to an earlier filed application, held that a disclosure lacking the teaching of how to use a fully

disclosed compound for a specific, substantial utility or of how to use for such purpose a compound produced by a fully disclosed process may be non-enabled under §112 but still be available as an anticipatory reference under §102. §112 provides that the specification must enable one skilled in the art to use the invention whereas §102 makes no such requirement as to an anticipatory disclosure.

Thus, a reference must itself be enabled and must enable the claimed invention to be adequate to support an anticipation rejection.

Obviousness

A finding of obviousness must be based on four underlying factual determinations:

- (1) The scope and content of the prior art;
- (2) The differences between the prior art and the claimed invention;
- (3) The level of ordinary skill in the art; and
- (4) Objective considerations of non-obviousness such as commercial success,

long felt but unmet need, failure of others to make the invention, and the like. See, Graham v. John Deere Co., 148 U.S.P.Q. 459 (1966). Failure to make these determinations precludes the making of a prima facie case of obviousness.

The Patent and Trademark Office must make the necessary findings and provide an administrative record showing the evidence on which its findings are based and its reasoning in reaching its conclusion. See, In re Zurko, 258 F.3d 1379, 59 U.S.P.Q.2d 1693, 1697 (Fed. Cir. 2001). When patentability turns on the question of obviousness, the search for and analysis of the prior art must include evidence relevant to the finding of whether there is a teaching, motivation or suggestion to select and combine the references relied on as evidence of obviousness. See, In re Sang Su Lee, 277 F.3d 1338, 61 U.S.P.Q.2d 1430 (Fed. Cir. 2002)

citing, *McGinley v. Franklin Sports, Inc.*, 262 F.3d 1335, 60 U.S.P.Q.2d 1001, 1008 (Fed. Cir. 2001). There must be a reason to combine the references. The reason to combine references must be based on objective evidence of record. Prior to *KSR International Co. v. Teleflex, Inc.*, 550 U.S. ____, 127 S. Ct. 1727 (2007), the Federal Circuit required that there be a showing of a suggestion, teaching or motivation to combine the prior art references as an essential component of an obviousness holding. *C. R. Bard, Inc. v. M3 Systems, Inc.*, 157 F.3d 1340, 48 U.S.P.Q.2d 1225, 1232 (Fed. Cir. 1998). Although the Supreme Court rejected this rigid requirement the test is still alive and can be used to provide helpful insight. The Patent and Trademark Office has advised its examiners that this test will still be used in obviousness evaluations and the patent examiner still needs to look for specific reasons why the prior art would be combined into a new patent before rejecting applications for obviousness.

Particular findings must be made as to the reason why a skilled artisan with no knowledge of the claimed invention would have selected the components for combination in the manner claimed. *In re Kotzab*, 217 F.3d 1365, 55 U.S.P.Q.2d 1313, 1317 (Fed. Cir. 2000). The Patent and Trademark Office must identify specifically the principal known to one of ordinary skill, that suggests the claimed combination. *In re Rouffet*, 149 F.3d 1350, 47 U.S.P.Q.2d 1453, 1459 (Fed. Cir. 1998). The Patent and Trademark Office must explain the reasons why one of ordinary skill in the art would have been motivated to select the references and to combine them to render the claimed invention obvious. Further, the Patent and Trademark Office can satisfy the burden of showing obviousness of the combination only by showing some objective teaching in the prior art or that knowledge generally available to one of ordinary skill would lead that individual to combine the relevant teachings of the references. See, *In re Fritch*, 972 F.2d 1260, 23 U.S.P.Q. 1780, 1783 (Fed. Cir. 1992). The factual question of motivation is material to

patentability and cannot be resolved on subjective belief and unknown authority. It is improper in determining whether a person of ordinary skill would have been led to this combination of references simply to “use that which the inventor taught against the teacher.” *W. L. Gore v. Garlock, Inc.*, 721 F.2d 1540, 220 U.S.P.Q. 303, 312-13 ((Fed. Cir. 1983). The Patent and Trademark Office must examine the relevant data and articulate a satisfactory explanation for its action or position including a rational connection between the facts found and the choice made. *Motor Vehicles Manufactures Association v. State Farm Mutual Automobile Ins. Co.*, 463 U.S. 29, 43 (Sup. Ct. 1983).

Where a trade off between features is required to produce an invention from a combination of references, motivation to combine requires the tradeoff be desirable not just feasible. See, *Winner International Royalty Corp. v. Wang*, 202 F.3d 1340, 53 U.S.P.Q.2d 1580 (Fed. Cir. 2000).

It has been held that supporting a rejection on common knowledge and common sense is inappropriate. Reference to common knowledge without evidence in support or explanation in support is inappropriate. See, *Smiths Industries Medical Systems, Inc. v. Vital Signs, Inc.*, 1836 F.3d 1347, 51 U.S.P.Q.2d 1415, 1421 (Fed. Cir. 1999). Failure to articulate an appropriate reason for the rejection is fatal to the position of obviousness. The Patent and Trademark Office cannot merely make conclusory statements when dealing with particular combinations of prior art but must set forth the rationale on which it relies. *In re Sang Su Lee*, *supra*. Thus, it is improper to state a combination is within ordinary skill in the art without support.

An appropriate analysis in the determination of obviousness may not indulge in forbidden hindsight evaluation. “Our case law makes clear that the best defense against the subtle but powerful attraction of a hindsight-based obviousness analysis is rigorous application of the

requirement for a showing of the teaching or motivation to combine prior art references. *In re Dembiczak*, 175 F.3d 994, 50 U.S.P.Q.2d 1614, 1617 (Fed. Cir. 1999). It has also been held that teachings of references can be combined only if there is some suggestion or incentive to do so. See *ACS Hosp. Sys., Inc. v. Montefiore Hosp.*, 732 F.2d 1572, 221 U.S.P.Q. 929, 933 (Fed. Cir. 1984). (It is yet unclear if these tests will withstand the Supreme Court decision in *KSR International Co.*, supra.)

Another important consideration in the determination of obviousness is who is one of ordinary skill in the art and what is the level of ordinary skill in the art. One cannot determine if an invention would have been obvious to one of ordinary skill in the art without first determining who that person would be. Several factors are evaluated to determine the level of ordinary skill. Those factors include: 1) the types of problems encountered in the art; 2) the prior art solution to those problems; 3) the rapidity of innovation; 4) the sophistication of the technology; and 5) the educational level of active workers in the field. See *Ruiz v. A.B. Chance Co.*, 234 F.3d 654, 57 U.S.P.Q.2d 1162 (Fed. Cir. 2000).

The Examiner must review all prior art even that art which will not support the rejection. See Section 706 MPEP and *Panduit Corp. v. Dennison Mfg. Co.*, 774 F.2d 1082, (Fed. Cir. 1985). Further, the Patent and Trademark Office cannot pick and choose between references or teachings in references. See *In re Wesslau*, 353 F.2d 238 (CCPA 1965). See also *Dennison Mfg. Co. v. Panduit Corp.*, 475 U.S. 809, 106 S.Ct. 1578, 89L.Ed. 2d 817 (S.Ct. 1986).

The court in the *Gillette Company v. S.C. Johnson & Son, Inc.*, 919 F.2d 720 (Fed. Cir. 1990) held that it is improper to focus on the obviousness of substitutions and differences instead of on the invention as a whole.

The Federal Circuit held in *In re Peterson*, 315 F.3d 1325 (Fed. Cir. 2003) that an applicant may rebut a prima facie case of obviousness by showing that the prior art teaches away from the claimed invention in any material respect. The court cited to *In re Geisler*, 116 F.3d at page 1469 (Fed. Cir. 1997) and to *In re Malagari*, 499 F.2d at page 1333 (CCPA 1974). See also MPEP §§ 2142, 2143, 2144 and 2145.

Arbitrary and Capricious Action

Reasoned findings are critical to the performance of an agency's functions and judicial reliance on agency findings. Absent reasoned findings based on substantial evidence, effective review would become lost in the haze of so called expertise. See *Baltimore and Ohio Railroad Co., v. Aberdeen & Rockfish Railroad Co.*, 393 U.S. 87, 91-92 (Sup. Ct. 1968).

The Federal Circuit Court of Appeals, in *In re Sang-Su Lee*, 277 F.3d 1338 (Fed. Cir. 2002) explained the duties of the United States Patent and Trademark Office in making findings in support of their decisions. Conclusory statements without the proper support are not adequate to support an agency's findings. A factual question cannot be resolved on subjective belief and unknown authority. The PTO must not only assure that the requisite findings are made, based on evidence of record, but must also explain the reasoning by which the findings are deemed to support the agency's conclusion. The court cites to 5 U.S.C. §706(2) stating that the reviewing court shall hold unlawful and set aside any agency actions, findings and conclusions found to be arbitrary, capricious, an abuse of discretion or otherwise not in accordance with law. The Administrative Procedure Act requires that an agency not only have reached a sound decision but have articulated the reasons for that decision. The agency must provide an administrative record showing the evidence on which the findings are based accompanied by the agency's reasoning in reaching its conclusions. These must be found within the four corners of the record.

Presumptions are not adequate. Mere conclusions will not suffice. The court further held that a decision by an agency tribunal that has an omission of a relevant factor required by precedent is both legal error and arbitrary agency action. Most importantly the court stated that an agency is not free to refuse to follow precedent. The Examiner, cites to case precedent to support her positions but ignores on point precedent regarding the use of a term like molded along with her own earlier actions approving the use of such structural terms. The Patent and Trademark Office cannot have it both ways.

The court in *Garrett v. FCC*, 513 F.2d 1056 (CA DC 1975) addressed the denial of a change to a radio station license and a claim of disparate decisional treatment by an administrative body. The court stated that they have twice said that an agency cannot act arbitrarily nor can it treat similar situations in dissimilar ways. “...(T)hat agency action cannot stand when it is “so inconsistent with its precedents as to constitute arbitrary treatment amounting to an abuse of discretion.” The court further held “It is clear, however, not only that ‘[m]ore than enumeration of factual differences between cases is required,’ but also that “the commission must explain their relevance to the purpose of the ‘legislation’ it administers. ... It is a simple but fundamental rule of administrative law ... “that a reviewing court, in dealing with a determination or judgment which an administrative agency alone is authorized to make, must adjudge the propriety of such action solely by the grounds invoked by the agency.” ...We cannot accept rationalizations offered by counsel as an adequate substitute for a response due the commission itself. It is neither for counsel nor for us, but for the commission itself, to explain any distinguishing characteristics it finds appealing, and to do so on a basis demonstrative of their pertinence to its statutory responsibilities.”

In *Deaton, Inc. v. Interstate Commerce Commission*, 693 F.2d 128, 131 (CA 11 1982), a case involving a grant of authority to a trucking company, the court held, “Of course, to survive judicial review under the arbitrary and capricious standard, an agency must explain the rationale for its decision.”

In the case *Marco Sales Company v. Federal Trade Commission*, 453 F.2d 1 (CA 2 1971), the court addressed an issue of the FTC’s regulation of certain alleged gambling activities. The court held ... “[o]n the other hand, as the *Moog Industries* case also indicates, the FTC does not have unbridled power to institute proceedings which will arbitrarily destroy one of many law violators in an industry. The arbitrary character of the Commission’s action here consists of its total failure to even advert to, much less explain, its reason for the rigid ad hoc adjudicatory stance it adopted toward the petitioner and the flexible tolerance its industry regulation displayed to those utilizing the same or similar devices ... But law does not permit an agency to grant to one person the right to do that which it denies to another similarly situated. ... Section 8(b) of the Administrative Procedure Act (5 U.S.C. §557(c)) requires an agency in any case to include in its decision its findings and conclusions as well as the reasons or basis therefor. This requirement takes on added importance when the decision is apparently inconsistent with the virtually contemporaneously declared rule. ... That an administrative agency is obligated to provide petitioner with an explanation for the difference in their treatment, is well established.”

Complete Prosecution

An examiner must provide reasoning for the rejection and cite to material(s) used to support the rejection. MPEP §706 and 37 CFR 1.104. According to MPEP §706.07(c) a premature final rejection cannot be appealed. However, this is purely a question of practice wholly apart from the tenability of the rejection. According to 37 CFR 1.113 a final rejection,

good or bad, can be made on the second or any subsequent consideration of the claims, and, according to MPEP §706.07(a) that any second action “shall be final, except where the examiner has introduced a new ground of rejection . . .”. Thus, unless a new reference is cited, the second action must be final and is thus an appealable action.

8. Arguments

The first three rejections, as noted above, are new rejections applying new references Rochlis, Akeno and Clune. It is submitted that making of the new Office Action a final rejection is inappropriate as being premature. Any objection to prematurity is waived. In view of the length of time that prosecution has gone forward, the number of Office Actions received, the number of Appeal Briefs filed, the following arguments are provided to advance prosecution in a timely manner.

Solely for purposes of simplifying this appeal, the patentability of dependent claims 2, 3, 5-10, 12-14, 35-46 rises or falls on the patentability of their respective independent claims.

The issues presented on appeal include:

1. Whether the claims are anticipated under 35 USC §102(b) or (e) by various of the above-referenced patents;
2. Whether the claims rejected as being obvious under 35 USC §103(a) are obvious over various of the above-referenced patents;
3. Whether or not complete prosecution has been provided in the new Final Office Action; and
4. Whether the Examiner's lack of action and positions taken in this case are arbitrary and capricious in that they are different from earlier actions taken by the Examiner in other applications and fail to follow precedent, in particular:
 - (a) whether or not some claim terminology is structural or process;
 - (b) whether or not the phrase integrally molded thermoplastic structure is a structural phrase; and

(c) whether the subject phrase converts an apparatus/structure claim to a product by process claim.

By way of background, each of the applied references is briefly discussed below.

Rochlis is directed to an apparatus and a molded product having staggered molded pile. The product has a base layer and pile with the pile being either uniform or non-uniform in height and/or shape. The pile layer may be formed on a laminated second layer. The Examiner has concluded, in citing to lines 61-75 of column 9 through line 23 of column 10, that this patent teaches the use of different polymers at the same time. However, it is respectfully pointed out that the only disclosure in this section, or anywhere else in the patent for that matter, relates to using ingredients having a different hardness. It is pointed out, that the change in hardness is not necessitated by a change in polymers. First, one must distinguish a molding material (as Rochlis describes) from a polymer contained therein. A molding material is not necessarily and rarely is a pure polymer. It can, as pointed out by the Examiner, include fillers, colorants which can affect properties of the molding material. Additionally, different plastecizers, and other additives to the polymer and temperature can affect its "hardness". There is simply no disclosure in Rochlis of using different polymers at the same time to make an individual article. It is respectfully requested that the Examiner point to any specific disclosure in Rochlis that specifically teaches the use of different polymers (not molding materials that include a polymer) to form a single article, not different polymers to form different articles but within the same article itself. None can be found and such disclosure is required.

Akeno discloses the formation of a hook structure apparently for use in Velcro type hook and loop fasteners. The hooks that are formed on the base layer have side rib portions for stiffening the hooks against lateral movement and falling over.

Clune teaches the formation of molded fastener elements extending from a common base. The Examiner is correct in the Examiner's characterization of Clune that it teaches the use of thermoplastic polymers which are suitable for molding fastener elements that include both polyethylene and polypropylene.

Sallee is directed to a garnish which is comprised of a perforated mat having a plurality of tufted filaments or strips attached to the mat which is camouflaged. It is specifically desired, as pointed out at column 2 starting at line 35, that the tufts be interchangeable so as to provide for variable patterns of shape and color to garnishes. The device is specifically devised to reduce thermal image. The device is complicated in structure, time consuming to assemble and is used on vehicles for disguising the vehicle. It is also disclosed at column 5 starting at line 37 that the attachment of the tufts may be permanent or more preferably they are releaseable and reattachable which means that the tuft are formed separately from the base layer, a requirement contrary to the present invention. There is no disclosure on how the attachment can be made permanent or what, in context, permanent means, but all forms of attachment described are of a mechanical locking type which are in and of themselves, as disclosed and as conceded by the Examiner, permanent. Regardless, the tufts are only disclosed as being attached to the tuft anchors by adhesion. The Examiner has read into this reference structural particulars that are not disclosed.

Nesbitt discloses a removable camouflage material or panel for use on magnetic vehicles for example, those having a steel body. It is disclosed that the base material can have a magnetic material in it for assisting adhesion of the panel to the vehicle. Nowhere is it disclosed that this increases slip resistance as contended by the Examiner. Slip resistance would normally mean the material has an increased coefficient of friction. The addition of magnetic material to an

elastomer has not been established as increasing the coefficient of friction between that material and another material. Since improved slip resistance is not disclosed, and only concluded by the Examiner and thus unique knowledge to the Examiner, an affidavit under 34 CFR 1.104(d)(2) is requested.

Rawlinson has been cited by the Examiner for the proposition that it would be obvious to use a polyethylene having a density between 0.915 and 0.92. For the purposes of this Appeal, this is conceded to the Examiner. Sesselmann is cited for the proposition that it would be obvious to add alumina as a filler material for the polymer to form a molding material. For the purposes of appeal, this issue is conceded to the Examiner. However, it is respectfully pointed out that the present invention is not related to odor reduction.

Claims 34-39, 41-44 – §102(b) rejection over Rochlis

Of this group of claims, Claim 34 is the only independent claim. For purposes of this appeal, the patentability of Claims 35-39, 41-44 rise or fall on the patentability of Claim 34. It specifies that a first plurality of projecting element portions are formed of a first polymer material and a second plurality of projecting elements are formed of a second polymer material and that the first plurality of projecting element portions and the second plurality of projecting element portions being an integrally molded thermoplastic structure. The Examiner concludes without any support or any explanation that because Rochlis discloses that the projecting elements can be formed so that they have different colors that this meets the limitations of the projecting elements being made from different polymers. (It is noted that a color change is effected by an additive such as a pigment.) Nowhere has Examiner provided any support for this conclusion. Colors are not typically thermoplastic polymers but are additives to thermoplastic polymer based molding compounds. For example, it is pointed out by the Examiner that

titanium dioxide is a colorant and it is not a thermoplastic polymer. The Examiner goes on to explain that because the projecting elements may be different in their hardness or other characteristics that they are of different polymers. Again, no support or technical explanation has been provided for this conclusion, merely the Examiner's opinion. It is respectfully requested that the Examiner provide an affidavit under 37 CFR 1.104(d)(2) to substantiate the Examiner's personal knowledge since there is no such information contained within the four corners of Rochlis and Rochlis only discusses the molding material properties, not the properties of the molding material components such as the polymer.

It is respectfully pointed out, that many things can affect hardness of the molding material which includes the polymer and other ingredients. For example, the type and amount of filler, the type and amount of plasticizer. In addition, a careful reading of Rochlis talks about the hardness as being affected by the temperature of the material which can be affected by the material's color or when the material is added during the molding process which will determine its temperature. Hardness can be changed by the amount of preheat applied to the molding compound. Although Rochlis is silent, some molding materials are pre-heated before molding which will affect hardness. Since temperature increase is a time related function and the time in contact with a heated mold or a cooled mold affects the molding material's temperature and hence its hardness. Thus, each and every element of Claims 34-39, 41-44 is not disclosed by Rochlis and therefore the anticipation rejection must fail.

Claims 1-5, 7, 9-13, 15, 47 – 35 USC §103(a) – Rochlis in view of Akeno, et. al.

The Examiner contends that the subject claims are obvious over Rochlis in view of Akeno, et. al. The basis for this rejection is that because the projecting elements of Rochlis can have different color, that meets the limitation of the projecting elements being made from

different polymers. The Examiner also concludes that if the elements have different hardnesses, they are also of different polymers. These issues were discussed and discredited in the preceding rejection discussion. Of this group of claims, Claims 1 and 47 are independent containing similar distinguishing elements and are treated together, i.e., the structure of the projecting elements. Claims 4, 11 and 15 depend from Claim 1 and further specify a plurality of the projecting elements.

Claims 1, 47

Claim 1 requires there should be at least one projecting element portion having a lower part and a terminal part. The lower part includes a core and a surface wherein the core and the terminal part of the projecting element portion are formed of a first polymer material and the surface is formed of a second polymer material. No such structure is disclosed by Rochlis or Akeno and thus, the rejection fails. It is not clear from the rejection whether it is the Rochlis structure or the Akeno structure that provides the structure of different polymers in the projecting element. To add further to the confusion, the Examiner at page 3 of the rejection states that it would be obvious to modify the projecting elements of Rochlis so that they have the structure of the projecting elements of Akeno in order to provide a reinforced hook fastener. There is no limitation in the rejected claims relating to reinforced elements. It is not clear what this portion of the rejection means and is therefore deficient. The Examiner then goes on to further state that it would have been obvious to have employed different polymers which differ in color, hardness, etc. as taught in Rochlis in order to form a material which had an improved appearance (not claimed), strength (not claimed), etc. This dissertation provides even more confusion resulting in incomplete prosecution for failure to specifically articulate a rejection. The Examiner attributes this teaching to Rochlis, but there is no such teaching found in Rochlis. Rochlis does not teach

different polymers or where they are located and certainly not in a projecting element as Claim 1 and Claim 47 require.

Claims 4, 11, 15

Claims 4, 11 and 15 define a plurality of projecting elements and different pigments (Claims 4, 11) and at least one distinct polymer (Claim 15) which structure is also not taught by Rochlis and Akeno or their combination. Thus, even for an obviousness rejection, these two references are deficient in their teaching since they do not disclose claim elements which missing elements are not addressed by the Examiner. It is respectfully pointed out again, that the Examiner provide where in Rochlis or Akeno this teaching can be found.

Additionally, the specific limitations found in claims 4, 11 and 15 are not addressed in this rejection and it is submitted, therefore, that this portion of the rejection is incomplete and must be reversed. As discussed above, all limitations in claims 1 and 47 have not been addressed as required for a proper rejection notably, the multi-polymer construction of the projecting element(s).

Thus, these rejections must be reversed.

**Claims 8, 40, 45-46 – Obviousness Rejection under
35 USC §103(a) – Rochlis, Akeno, et. al. and Clune**

Firstly, these claims depend from allowable claims as discussed above and therefore are patentable for that reason alone. It is conceded, for the purposes of this Appeal, that the patentability of these claims rises or falls on the patentability of their respective independent claims.

Claims 1, 3, 5, 7, 8, 10-12, 34-40, 42-44
Anticipation under 35 USC §102(e) – Obvious under 35 USC §103(a) – Sallee

Claims 39, 42

Firstly, it is pointed out that there can be found no discussion directed to Claims 39 and 42 in the text of the rejection. Therefore, this rejection is deficient and must fail. However, this issue is moot since the patentability of these claims rises or falls on the patentability of Claim 34.

Claims 1, 11, 34

It is respectfully pointed out that Sallee does not disclose the use of the two polymers as required in the two independent claims and one dependent claim, namely Claims 1, 11 and 34, from which the other claims variously depend. (The remaining claims are conceded as rising or falling on the patentability of other claims.) Sallee does not disclose the use of two different polymers in an integrally molded structure. It is noted that, Claim 1 is not specifically identified in the discussion of the rejections nor is there any discussion of integrally molded in any text that might relate to Claim 1. There is only a discussion of what Sallee discloses in section 5 at page 5 of the rejection and this discussion does not mention many of the limitations contained in Claim 1, e.g., planar base with first and second sides, a projecting element with a core and a surface and a terminal part with the core and the terminal part being of different polymers and the integrally molded thermoplastic structure. Thus the rejection fails and, Claim 1 is allowable. The Examiner is required to articulate a complete rejection and discuss each claim element in the rejection. Claim 11 further defines that there are a plurality of projecting elements, a limitation not addressed in this rejection. This rejection must fail since prosecution is not complete. There is however a discussion of integrally molded as it relates to Claim 34 and some of its depending claims. The Examiner concedes, in discussing Claim 34 and its depending claims, at section 6 starting on page 6 of the Office Action that a molded structure is one produced by a molding

process, conceding to Applicant, or in the alternative, providing contradictory arguments that molded is not a structural term.

There is a discussion of the “integrally molded thermoplastic structure” limitation in the Examiner’s discussion of Claim 34.

It is contended once again that the phrase integrally molded thermoplastic structure is a structural term and not a product by process term. The Examiner concedes in section 6 that the instant claims are drawn to a product and not how the product is made again apparently conceding to Applicant that Applicant’s arguments that integrally molded thermoplastic structure is a structural term. The Examiner states on page 6 of the Final Rejection “The instant claims are drawn to a product and not to how the product is made.” The Examiner cites to what the Examiner claims to be process language, permanent attachment, to reject a product claim yet claims that process language does not define a product which means there is no disclosed product in Sallee to support, at least, the anticipation rejection of Claim 34 (and also Claim 1). The first portion of the rejection of Claim 34 is an anticipation rejection and the defined structure cannot be found in Sallee, i.e., that there are side by side areas of projecting elements formed of different polymers and that the structure is an integrally molded structure. Thus, the anticipation rejection fails.

The Examiner has not specifically identified Claims 1 and 11 in the rejection, however the above arguments apply to Claim 1. In addition, the defined core and the surface of the projecting element of Claim 1 are of different polymers, limitations which are not found disclosed in Sallee. Nor are the “integrally molded structure” limitations in Claim 1 and its depending claims discussed and they are not disclosed by Sallee.

It is pointed out that there is no discussion of or the required analyses for an obviousness rejection. In fact, outside of the initial statement of the rejection the analyses of the teachings and the claims does not once use either the word “obvious” or “obviousness”. The Examiner has not fulfilled the requirements of MPEP §§ 706.02(j) (particularly subparagraphs (B), (C) and (D1)) and MPEP § 2142. Thus, the obviousness rejection must fail for this reason alone. Additionally, this rejection fails for the same reasons as discussed above in that there is no disclosure in Saltee of elements in the claims and without more the reference will not support the rejection. The Examiner has not pointed out what Saltee does not teach in order to apply an obviousness rejection. Reasoning behind a rejection is required and has not been articulated. While there is a discussion in the rejection of Claim 34 and its depending claims of there being a permanent attachment taught by Saltee, there is no such discussion regarding Claim 1 and its depending claims. Then after discussing “attachment” in the rejection of Claim 34, the Examiner states the parts are “bonded” which is not disclosed. While Saltee does disclose a permanent attachment, it is not clear from the teaching of Saltee what this means. In column 5 of Saltee starting at line 37 it is disclosed that “The attachment to the base camouflage material 100 may be permanent or, more preferably, releaseable and reattachable, allowing removal and replacement of garnishes of the invention”. There is no disclosure of what “permanent” attachment is or might be. The paragraph talks about the anchor, the garnish, a barb and a device to secure the garnish to the camouflage material. Certainly, an integral molded structure is not disclosed which is conceded by the Patent and Trademark Office. Additionally, it is not clear how the attachment can be permanent (as the Examiner needs to establish to support the rejection) and the part still be removable for replacement as the sentence appears to state. Further, it is not clear what is attached to the base camouflage material in a permanent manner.

Sallee appears to require several wraps of the tuft about the anchor and how this could be a molded structure is not enabled as required. Given the need to be able to customize the tuft arrangement, this structure could not be an integrally molded structure and is contrary to the present invention. Given that the preferred material for the tuft is metallized Mylar and that there be multiple wraps to form a tuft it appears that a molded structure would not provide the disclosed structure. No disclosure has been cited and no discussion of how metallized Mylar can be part of an integrally molded structure. The metal of metallized Mylar is separately applied, e.g., as by vapor deposition after the Mylar component is formed. Specifically regarding Claim 34, there is no disclosure by Sallee of first projecting elements formed from a first polymer and second projecting elements formed from a second polymer and that those projecting elements are in a structure that is an integrally molded structure or, regarding Claim 1 that a projecting element has a core and a surface portion of two polymers. Thus, each and every claimed element is not disclosed by Sallee (therefore the anticipation rejection must fail) and without more, Sallee will not support an obviousness rejection either. No rationale has been provided on how it would be obvious to make the claimed invention from the teaching of Sallee because it does not disclose claimed elements or who is one skilled in the art to provide a proper basis for evaluation.

Because there is no discussion of obviousness provided in the rejection, the obviousness rejection must fail as being legally deficient. Because there is no discussion of obviousness, an argument countering obviousness cannot be provided, without speculation, since it is not clear what is or is not obvious. It is the job of the Patent and Trademark Office to provide proper rejections and not place on an Applicant the burden of speculating what the rejection might or

might not be. The Examiner is again invited to point out what the obviousness rejection comprises for the rejected claims.

Finally, with regard to this rejection, the Examiner argues that the courts have approved the rejection of product by process claims under 35 USC §102/103. It is contended once again, that the claims (except Claim 47) are not product by process claims but pure structure claims. In one stroke of the pen, the Examiner would destroy thousands of patents since they contain terminology related to process i.e., the verb form of a word, for example molded, bolted, welded, polymer (polymerized), etc. Whether or not such a rejection is imminently fair and acceptable is not relevant. The issue is simply whether or not the claims are anticipated or obvious. It is pointed out that there is no claim of a process in these claims as contended by the Examiner. In fact, this very Examiner has approved claims with such terms in them without objection which is discussed below in the section on Arbitrary and Capricious Action.

Claims 2, 4 – 35 USC §103(a) – Sallee in view of Nesbitt

For the purposes of this rejection, it is conceded that Claims 2 and 4 rise or fall on the patentability of Claim 1 from which they depend. However, it is pointed out that all the limitations of these claims are not discussed, i.e., those contained in Claim 1. Also, the second paragraph of the rejection discusses limitations not found in Claims 2, 4.

Claims 13, 45 – 35 USC §103(a) – Sallee in view of Rawlinson

For the purposes of this Appeal, it is conceded that Claims 13 and 45 rise or fall on the patentability of the claims from which they depend.

Claims 14, 46 – 35 USC §103(a) – Sallee in view of Sesselmann

For the purposes of this Appeal, it is conceded that the patentability of Claims 14 and 46 rise or fall on the patentability of the claims from which they depend.

Arbitrary and Capricious Action

There is an issue that is common to all rejections, that is, whether or not the claim terminology, e.g., “integrally molded thermoplastic structure” is a structural term and thus distinguished from the cited references or whether it is a process step rendering the claim a product by process claim. It is pointed out that claims 1 and 34 are the classic article claim with the preamble so indicating. Claim 47 was added as a true product by process claim. In this regard, the Board’s attention is directed to the following. In the case *Pen Tec, Inc. v. Graphic Controls Corp.*, 224 U.S.P.Q. 976 (DC CD CA 1984), a case directly on point and involving almost identical claim language, the court treated the phrase “integrally molded hinge member” as a structural term and distinguished the claim language from hinges that had separate members. The Examiner has refused to acknowledge or discuss this case even though it was cited during prosecution. Distinguish or follow, but the Examiner is without authority to ignore or overrule. In further support of the subject claim language defining structure, the Examiner prosecuting this case has issued several patents apparently without objection to the claims being product by process claims but rather viewing them as structure claims. In U.S. Patent 7,172,802, Claim 1 includes the following terms which are similar to those objected to by the Examiner in the subject application. Those terms include woven, pigmented and polymer. Woven is a structural term as is pigmented. A polymer is formed by the process of polymerization but is “structural” in meaning or designates “type”. These terms in context define “structure” and/or “type” not process. In U.S. Patent 7,041,355, Claim 1 contains the terms molded shell, polymer and heat activated expandable adhesive. In U.S. Patent 7,132,161, this Examiner approved electroflocked, bonded and “second fibers being arranged and configured.” In U.S. Patent 6,982,231, this Examiner approved a structure claim directed to a laminate that used the words

bonded, stretched, breathability and non-woven. The position now taken by the Patent and Trademark Office raises serious issues of violation of the Due Process Clause under the Fifth Amendment and violation of the Administrative Procedures Act that forbids arbitrary and capricious actions.

The issue of the meaning of the phrase “integrally molded thermoplastic structure” has yet to be discussed by the Patent and Trademark Office except to dissect the phrase and look at each individual word and then out of context. The use of “integrally molded thermoplastic structure” is as much structure as words commonly found in claims for example, bolted, fastened, laminated, welded, secured and many others including those approved by this Examiner. Numerous words used in patents and patent claims have both a verb or action form and a structure or noun form. Some of these have just been mentioned. The use of such words permits of economy of words, clarity and definiteness. How would one define a welded structure without using “welded”? This issue has been raised during prosecution and no substantive response has been received. The Patent and Trademark Office, with a single stroke of the pen, would potentially invalidated thousands of patents with its position and has cited to no relevant authority that the subject language (or similar language) converts the claims to product by process claims. The rationale is thus only within the personal knowledge of the Examiner and an affidavit under 37 CFR 1.104(d)(2) is respectfully requested.

Thus, a principal issue presented to the Board is whether or not the phrase “integrally molded thermoplastic structure” is a structural term or if the phrase converts a claim to a product by process claim as alleged by the Patent and Trademark Office. It is submitted that the phrase is structural and therefore clearly distinguishes all the claims over the cited references. The Examiner apparently recognizes this weakness in the prior rejections by newly citing to Rochlis

which does disclose an integrally molded structure, just not the claimed structures. Since none of the other references, as conceded by the Patent and Trademark Office, show an integral molded structure, the phrase “integrally molded thermoplastic” is an adjectival phrase modifying “structure” defining the specific type of structure as would the phrase woven cloth or welded assembly. The rejections are thus in error and must be reversed. The subject phrase cannot be dissected and a meaning given to each individual word. To do so is error and inconsistent with prior Patent and Trademark Office practices as evidenced by patents issued by this very Examiner.

The Examiner has conceded that some of the cited references do not disclose an integral molded structure. Recognizing the problem with this, the Examiner then concludes without authority, that the claims are product by process claims and the process to make the product is not a claim limitation. In fact, if one reviewed the dictionary for “molding” they would find that molding is both a verb i.e., performing the act of molding and the name of a thing, a molding, the thing produced by act of molding. One must look to the context of use to determine what is meant by the word. The Examiner cites to *In re Marosi, et. al.*, 216 USPQ 289, 292 (Fed. Cir. 1983) as authority. That case appears to have involved a true product by process claim and that law for such a claim is good law. However, Claims 1 and 34 and their depending claims are not product by process claims and the Examiner has cited to no relevant authority to support that these claims are product by process claims. It is requested that the Examiner provide such authority and distinguish her own prior actions. The trite, and over used phrase, that “each case is judged on its own” while possibly true, cannot be used to avoid precedent or providing the required explanation for a proper rejection. Again, distinguish or follow precedent.

It is respectfully submitted that the rejections of the claims are in error. It is further submitted that numerous of the claims have not been properly rejected particularly many of the obviousness rejections.

It is respectfully requested that the Board reverse the Examiner on all the rejections or in the alternative, remand this case back to the Examiner for proper prosecution.

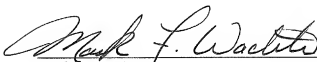
9. Conclusions

It is clear that the rejections of the claims must be reversed. It is also respectfully requested that this Board find that the phrase "integrally molded thermoplastic structure" is structural as used in the claims and that the Patent and Trademark Office has violated its obligations under the Administrative Procedures Act and the Fifth Amendment Due Process Clause.

Respectfully submitted,

Date:

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ATTORNEYS FOR APPLICANT

Appendix A – Claims Appendix

1. A three-dimensional polymeric article comprising a generally planar base portion having a first side and a second side and at least one projecting element portion having a lower part and a terminal part, with said projecting element portion extending from said first side of the generally planar base portion, wherein said lower part of said projecting element portion includes a core and a surface wherein said core and said terminal part of said projecting element portion are formed therethrough of a first polymer material and said surface is formed of a second polymer material, wherein said generally planar base portion and said projecting element portion being an integrally molded thermoplastic structure.

2. The article according to claim 1, wherein the first polymer material contains a first colored pigment and the second polymer material contains a second colored pigment.

3. The article according to claim 1, wherein the base contains a pigment that is different from the terminal part of the at least one projecting element.

4. The article according to claim 2, wherein the at least one projecting element includes a plurality of projecting elements each having a terminal part, wherein the base and a portion of the plurality of terminal parts for the plurality of projecting elements contain the same pigment and a portion of the plurality of terminal parts for the plurality of projecting elements contain a different pigment than the base.

5. The article according to claim 1, wherein the first polymer material and the second polymer material are polymers selected from the group consisting of polyolefins, polyethylene, polypropylene, vinyl polymers, polystyrene, styrene-acrylonitrile copolymers, styrene-butadiene copolymers, acrylonitrile-butadiene-styrene graft copolymers, polyvinyl

butyral, polyamides, nylon-6, nylon-6,6, thermoplastic, urethane polymers, thermoplastic elastomers, blends and alloys thereof.

7. The article according to claim 1, further comprising at least one from the group consisting of dyes, pigments of distinct colors and other fillers.

8. The article according to claim 1, wherein at least one of the first polymer material and the second polymer material is polyethylene.

9. The article according to claim 1, further comprising a slip-resistant sheet laminated to the base.

10. The article according to claim 1, wherein the base includes open spaces to facilitate cleaning.

11. The article according to claim 7, wherein the at least one projecting element includes a plurality of projecting elements and the base contains a pigment that is different from at least a minority of the plurality of projecting elements.

12. The article according to claim 7, wherein the base contains a distinct pigment.

13. The article according to claim 1, wherein at least one of the first polymer material and the second polymer material comprises polyethylene with a density in the range of between about 0.915 and about 0.92.

14. The article according to claim 1, further comprising at least one dispersed functional filler selected from the group consisting of minerals, alumina, metal oxides, conductive fillers and conductive polymers.

15. The article according to claim 1, wherein the at least one projecting element includes a plurality of projecting elements each having a terminal part and at least some of the plurality of terminal parts are formed from at least one distinct polymer.

34. A three-dimensional polymeric article comprising a generally planar base portion having a first side and a second side and at least one first plurality of projecting element portions and at least one second plurality of projecting element portions, each having a lower part and a terminal part and extending from said first side of the generally planar base portion, wherein said first plurality of projecting element portions are formed of a first polymer material and said second plurality of projecting element portions are formed of a second polymer material, wherein said generally planar base portion, said first plurality of projecting element portions and said second plurality of projecting element portions being an integrally molded thermoplastic structure.

35. The article according to claim 34, wherein the first polymer material contains a pigment of a first color and the second polymer material contains a pigment of a second color.

36. The article according to claim 34, wherein the base contains a pigment that is different from the at least one first plurality of projecting elements.

37. The article according to claim 34, wherein the base contains a pigment that is different from the at least one second plurality of projecting elements.

38. The article according to claim 34, wherein the first polymer material and the second polymer material are polymers selected from the group consisting of polyolefins, polyethylene, polypropylene, vinyl polymers, polystyrene, styrene-acrylonitrile copolymers, styrene-butadiene copolymers, acrylonitrile-butadiene-styrene graft copolymers, polyvinyl butyral, polyamides, nylon-6, nylon-6,6, thermoplastic, urethane polymers, thermoplastic elastomers, blends and alloys thereof.

39. The article according to claim 34, further comprising at least one from the group consisting of dyes, pigments of distinct colors and other fillers.

40. The article according to claim 34, wherein at least one of the first polymer material and the second polymer material is polyethylene.

41. The article according to 34, further comprising a slip-resistant sheet laminated to the base.

42. The article according to claim 34, wherein the base includes open spaces to facilitate cleaning.

43. The article according to claim 39, wherein the base contains a pigment that is different from at least a minority of the plurality of projecting elements.

44. The article according to claim 39, wherein the base contains a distinct pigment.

45. The article according claim 34, wherein at least one of the first polymer material and the second polymer material comprises polyethylene with a density in the range of between about 0.915 and about 0.92.

46. The article according to claim 34, further comprising at least one dispersed functional filler selected from the group consisting of minerals, alumina, metal oxides, conductive fillers and conductive polymers.

47. A multi-color mat comprising a generally planar base portion having a first side and a second side, the first side having a plurality of elements projecting therefrom each of the elements having a proximal end portion integral with the base portion and a terminal end portion integral with a respective proximal end portion, said proximal end portions having an internal core portion and an external surface portion, each said terminal end portion and respective core portion being formed of a first polymer material and the respective external surface portion being formed of a second polymer material, said mat being prepared by a process comprising the steps of:

- a) molding the base and surface portions as an integral structure; and
- b) molding the cores and respective terminal end portions each as an

integral structure that is integral with a respective proximal end portion.

Appendix B – Evidence Appendix

U.S. Patents:

7,172,802

7,041,355

7,132,161

6,982,231



US007172802B2

(12) **United States Patent**
Sutherland et al.

(10) **Patent No.:** **US 7,172,802 B2**
(45) **Date of Patent:** **Feb. 6, 2007**

(54) **CASEMENT FABRICS**

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(*) **Notice:** Subject to any disclaimer, the term of this
patent is extended or adjusted under 35
U.S.C. 154(b) by 957 days.

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(22) **Filed:** Dec. 27, 2001

(65) **Prior Publication Data**
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(51) **Int. Cl.**
B32B 3/10 (2006.01)

(52) **U.S. Cl.** 428/131; 442/49; 442/131;
442/301; 442/302; 442/2; 428/134; 139/417;
139/418

(58) **Field of Classification Search** 442/131;
442/301, 302, 2, 49; 428/131, 134; 139/417;
139/418

See application file for complete search history.

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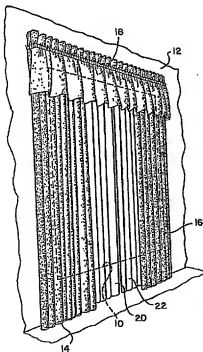
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(57) **ABSTRACT**

Window coverings are formed of woven fabrics of acrylic yarns to provide minimal degradation of the window covering due to ultraviolet (UV) radiation and to minimize damage to interior furnishings within a building at which the window coverings are applied. The window coverings are preferably formed of panels of pigmented acrylic yarn having a yarn number of about 24, 2 ply and a weave density of about 29 ends per inch of warp threads and 24 picks per inch of weft threads with about 0.063 inch square openings between the thread rows. UV blocking for A and B wavelength ranges may be on the order of 69 to 78 percent.

8 Claims, 1 Drawing Sheet



U.S. Patent

Feb. 6, 2007

US 7,172,802 B2

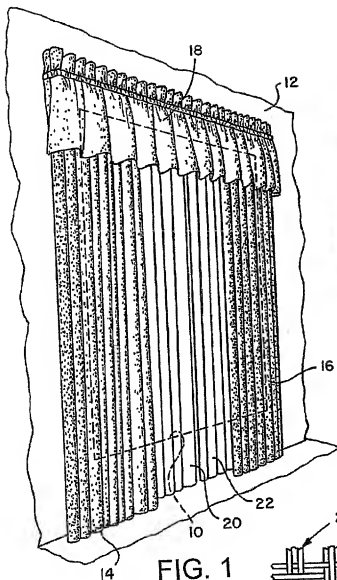


FIG. 1

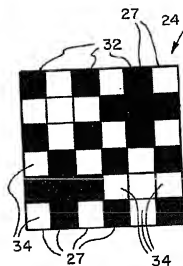


FIG. 3

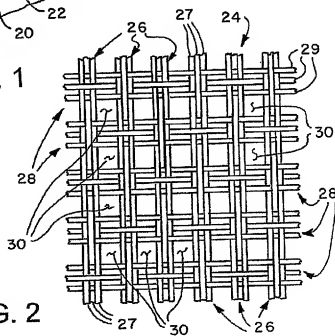


FIG. 2

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CASEMENT FABRICS

BACKGROUND OF THE INVENTION

Ultraviolet light sources, such as sunlight, are particularly detrimental to many articles of manufacture whether such articles be made of natural or man-made materials. For example, sunlight is particularly detrimental to window coverings and furnishings within a residential dwelling as well as commercial buildings of all types.

Accordingly, it is desirable to minimize the damage to the structure and appearance of certain articles, such as window coverings, carpeting and furnishings within a dwelling or other type of human occupied building, while at the same time allowing sufficient light to the room or rooms of the building to satisfy human needs as well as aesthetic qualities or characteristics of the room. For example, window coverings known as sheers are hung in many windows in addition to completely opaque window coverings, such as draperies and the like, to allow light to enter the room and to also permit humans occupying the room to see through the fabric of the sheers to the outside world. However, heretofore, fabrics used for and the light transmitting characteristics of known types of sheers have been unsuitable to prevent damage from ultraviolet radiation or light to the sheers themselves, as well as to opaque window coverings and the furnishings within the room at which the window coverings are hung.

Taking into account the vast number of residential dwellings, commercial office buildings, hotels and other buildings which are windowed and suffer from damage due to ultraviolet light, there has been a substantial need to provide improved window coverings which will reduce such damage while at the same time providing for admission of substantial natural light into the interior of the dwelling or building and to permit human occupants to see through the window coverings to the outside world.

SUMMARY OF THE INVENTION

The present invention provides an improved fabric particularly useful as a window covering for admitting artificial and, particularly, natural light into a room or rooms while allowing human occupants to see through the window covering, which window covering is also operable to substantially reduce the amount of ultraviolet light (radiation) which is admitted to the room through the window covering to thereby minimize damage from such radiation to articles of manmade and natural materials.

In accordance with one aspect of the present invention an improved fabric, particularly adapted for a window covering or the like, is provided which is formed of a woven material. The threads of the woven material are preferably formed of staple fiber yarn of an acrylic polymer, and, in particular, a pigmented acrylic polymer. It has been determined that so-called pigmented acrylic polymer yarns are particularly resistant to damage from ultraviolet light. Moreover, fabrics formed of such yarns also have superior ultraviolet light absorption or reflectivity characteristics which, when such fabrics are used as window coverings, substantially reduce damage to the window coverings and articles within a room or rooms at which the window coverings are hung.

In accordance with a further aspect of the present invention an improved window covering is provided which allows the admission of substantial light through the window covering, and permits a desired amount of visibility through the window covering, while also blocking the transmission of a

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substantial amount of ultraviolet light through the fabric of the window covering. In a preferred embodiment of the invention the window covering is formed of woven yarns of acrylic. The fiber content of the yarn is preferably substantially one hundred percent pigmented acrylic which is so-called solution-dyed, and the fiber has a denier of about 2.0. The yarn also, preferably, has a yarn number of twenty-four and is 2 ply. The weave density of the fabric, which may be varied, is, preferably, 29 ends per inch at the warp while the weft or fill is 24 picks per inch. The weave structure is also, preferably, a three strand warp with preferably about 0.063 inch square openings between the warp and weft rows. The colors of the warp and weft or fill yarns may be varied to meet particular aesthetic requirements.

The fabric of the invention may be considered somewhat reminiscent of so-called mosquito netting. The fabric in accordance with a preferred specification of the invention has revealed a substantial capability for blocking or reducing the transmission of ultraviolet radiation therethrough. For example, the percentage of blocking of ultraviolet A radiation (UVA) is as high as about 76 percent while the blocking of ultraviolet B radiation (UVB) may be as high as about 78 percent. Moreover, the fabric can be treated with a suitable organic flame retardant and a stain protection finish without affecting its ability to reduce ultraviolet light transmission and without being deleteriously affected by ultraviolet light itself.

Those skilled in the art will further appreciate the advantages and superior features of the present invention upon reading the detailed description which follows in conjunction with the drawing.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is an interior perspective view of a typical residential or commercial building room having a window with window coverings in accordance with the present invention; FIG. 2 is a detail plan view showing the threads and the weave of a window covering or casement fabric article in accordance with the present invention; and

FIG. 3 is a schematic diagram showing the weave pattern in accordance with one preferred embodiment of the present invention.

DETAILED DESCRIPTION OF A PREFERRED EMBODIMENT

In the description which follows like elements are marked throughout the specification and drawing with the same reference numerals, respectively. The drawing figures may not be to scale and certain elements may be shown in schematic or generalized form in the interest of clarity and conciseness.

Referring to FIG. 1, there is illustrated a typical application of the casement fabric of the present invention as a window covering for a window 10 disposed in an exterior wall 12 of a building or residential dwelling. The window 10 is decorated by a conventional set of opaque window coverings such as drapery panels 14 and 16 which are hung in a conventional manner together with a valance 18. The window 10 is also covered by light admitting window coverings or sheers comprising one or more panels 20 and 22 which are also hung in a conventional manner between the window 10 and the opaque window coverings 14, 16, 18. The panels 20 and 22 are formed of an improved window covering fabric in accordance with the invention, which fabric is resistant to ultraviolet light (radiation) in both the

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3 UVA and UVB wavelength ranges. However, the window covering panels 20 and 22 also admit substantial light through the window 10 and into the interior of the room at which the window is disposed while allowing persons within the room to view the outside world in some detail through the window covering panels in their closed position, as shown.

Referring now to FIG. 2, a detail plan view of a portion of one of the window covering panels 20 or 22 is illustrated to show the general construction of the fabric which forms the panels 20 and 22. One preferred embodiment of fabric making up the panels 20 and 22 is illustrated in FIG. 2 and generally designated by the numeral 24. The fabric 24 is preferably formed of a so-called pigmented or solution dyed polymer yarn, and more preferably yarn formed of acrylic (acrylonitrile) fibers. Pigmented or solution dyed yarn is formed by adding a coloring agent to the polymer material and thoroughly mixing the coloring agent throughout the polymer material at the time the polymer material itself is formed, as compared with adding a coloring agent or dye to the polymer material after formation thereof. Acrylic yarn, so formed, is preferred for its resistance to degradation by ultraviolet light (radiation) as well as for its ultraviolet radiation (UV) absorbing or reflectivity capability in accordance with the invention. A fiber content of substantially all acrylic, solution-dyed, is preferred, the fibers having a denier of about 2.0. In the fabric 24 the yarn strands preferably have a count or yarn number of twenty-four and are 2-ply. The weave structure is preferably formed of groups 26 made up of three warp strands or threads 27 and groups 28 which are also each formed of three weft or fill strands or threads 29. The spacing of the threads is approximately twenty-nine ends per inch for the warp threads 27 and twenty-four picks per inch for the weft or fill threads 29, leaving approximately 0.063 inch square openings 30 between adjacent groups 26 and 28 of warp and fill threads. This weave structure provides a weight per lineal yard of approximately 5.5 ounces for the yarn description herein. FIG. 3 is a schematic diagram of the weave structure with the raised picks indicated for each thread or strand 27 by the dark squares 32 and the lowered picks for each thread or strand 27 indicated by the lighter squares 34.

A fabric having the specifications set forth hereinabove has been indicated to be capable of blocking ultraviolet (UV) light in the A category wavelength in a range of about 69 to 76 percent, depending on fabric color, while also being capable of blocking UV light in the B category wavelength in a range of about 74 to 78 percent. Accordingly, a light transmitting fabric in accordance with the present invention is not only resistant itself to damage from ultraviolet light but is capable of blocking a significant amount of UV light transmission therethrough while admitting a sufficient amount of light to be aesthetically pleasing and while also permitting reasonable visual acuity by persons viewing objects on the other side of the fabric from where the person is disposed. As previously mentioned, for aesthetic purposes, the colors of the warp threads and weft threads may be different and the colors of each thread in a group 26 or 28 may be different also.

Window covering panels 20 and 22 formed of the fabric 24 may be treated with a commercially available flame retardant and a stain protection finish, respectively. One preferred source of flame retardant is Schneider-Banks Co., Athens, Tex. The fabric edges may be suitably bound by conventional methods.

4 The weave structure for the fabric 24 may be varied. For example, the weave pattern may be a plain weave and the weave density may be varied to provide openings 30 of from 0.03 to 0.25 inches square. However, the weave structure with the warp threads alternating over/under/over and the weft threads alternating with under/over/under is indicated to be preferred to maintain structural integrity and UV blocking capability.

Although a preferred embodiment of the invention has been described in detail herein, those skilled in the art will recognize that various substitutions and modifications may be made to the casement fabric described without departing from the scope and spirit of the appended claims.

What is claimed is:

1. A light transmitting window covering panel formed of a fabric comprising staple fiber acrylic yarn, woven in groups of warp threads and groups of weft threads the fiber content of said yarn being about 100 percent pigmented acrylonitrile polymer, and the weave density being such as to provide openings between said groups of warp threads and said groups of weft threads of about 0.03 inches to 0.25 inches to provide human visual perception through said panel and blocking the transmission of ultraviolet light through said panel in A category wavelength in a range of about 69 percent to 76 percent and in B category wavelength in a range of about 74 percent to 78 percent.
2. The window covering set forth in claim 1 wherein: each group of warp threads comprises three threads disposed adjacent one another between said openings, respectively.
3. The window covering set forth in claim 1 wherein: each group of weft threads comprises three threads disposed adjacent one another between said openings, respectively.
4. The window covering set forth in claim 1 wherein: the yarn weight is not less than a yarn number of about 24.
5. The window covering set forth in claim 4 wherein: the yarn is 2 ply.
6. A light transmitting window covering panel comprising a an ultraviolet radiation resistant fabric formed of acrylic yarn woven in groups of warp threads and groups of weft threads, the fiber content of said yarn being about 100 percent pigmented acrylonitrile polymer, the yarn weight being not less than a yarn number of about 24 and the weave density of said fabric is such as to provide openings between groups of adjacent warp threads and groups of adjacent weft threads in a range of about 0.03 to .25 inches square to provide human visual perception through said panel and blocking the transmission of ultraviolet light through said panel in A category wavelength of at least about 69 percent and in B category wavelength of at least about 74 percent.
7. The window covering set forth in claim 6 wherein: each group of warp threads comprises three threads disposed adjacent one another between said openings, respectively.
8. The window covering set forth in claim 6 wherein: each group of weft threads comprises three threads disposed adjacent one another between said openings, respectively.

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Juras et al.

(10) Patent No.: **US 7,041,355 B2**
 (45) Date of Patent: **May 9, 2006**

(54) **STRUCTURAL REINFORCEMENT PARTS
 FOR AUTOMOTIVE ASSEMBLY**

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- (*) Notice: Subject to any disclaimer, the term of this
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 U.S.C. 154(b) by 243 days.

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B32B 9/00 (2006.01)
B32B 15/04 (2006.01)

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Primary Examiner—Elizabeth M. Cole

Assistant Examiner—Victor S Chang

(57) **ABSTRACT**

The present invention is a structural reinforcement part for use in automobile assembly comprising a molded shell substantially filled with a structural filler material and an expandable adhesive in contact with the exterior of the molded shell; wherein the structural filler material does not undergo or require any chemical reaction or expansion, after part installation or during automotive assembly. This simplified structural reinforcement part does not require the in-situ foaming process of the prior art and produces a strong lightweight structural member which can be adhered to the automotive skeleton via the expandable adhesive upon exposure to heat during automotive assembly. This structural member offers easy installation, since no bulk systems, pumps or additional equipment is required.

- (52) **U.S. Cl.** 428/71; 428/304.4; 428/317.1;
 428/318.4; 428/318.8; 428/343; 428/354

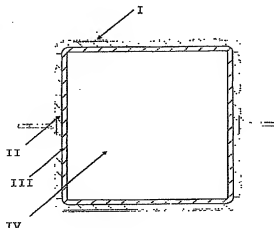
- (58) **Field of Classification Search** 428/71,
 428/304.4, 318.4, 318.8, 317.1, 343, 354
 See application file for complete search history.

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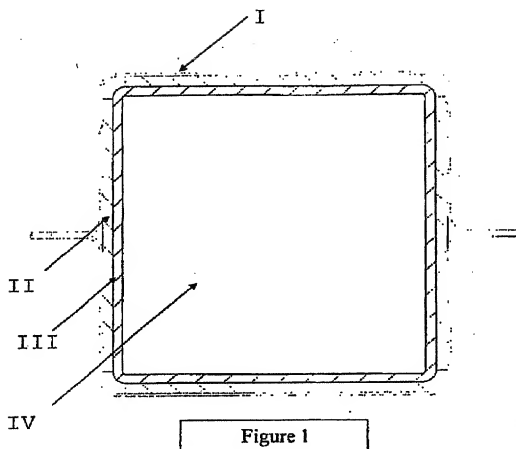
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STRUCTURAL REINFORCEMENT PARTS FOR AUTOMOTIVE ASSEMBLY

The present invention relates to structural reinforcement parts which are useful in automotive applications.

BACKGROUND

Reducing automotive vehicle weight, while maintaining safety and structural performance requirements, is a key design challenge facing automotive engineers. Minimizing vehicle mass is also essential in meeting increasingly stringent fuel economy, CAFE (Corporate Average Fuel Economy), and emission requirements. Engineers must find new methods, processes, and technologies to minimize vehicle weight without sacrificing engineering design requirements.

Conventional methods to improve body structure performance include modifying sheet metal thicknesses, modifying structure cross-section dimensions, and adding additional reinforcements and sheet metal pieces.

U.S. Pat. No. 5,194,199 discloses a structural part, such as a beam for vehicle construction, formed of a hollow metal member and a prefabricated reinforcing core of light-weight material. The part is produced by providing the core with a shell of heat-foamable material, and subjecting the assembly to a heated immersion-coating operation to expand the heat-foamable material. However this process requires a foaming shell which allows for uncertainty in the shape and size of the shell.

WO 01/55523 discloses a reinforcing member for a structural component comprising a carrier and a thermally expandable structural reinforcing material element. The thermally expandable reinforcing material is a synthetic resin which foams during high temperature baking in the automobile manufacturing process, (e.g. paint and powder coat bake stage). However, these foaming in-place processes are not preferred, due to the difficulty in controlling the core foam expansion path and direction, and also in minimizing foam usage and weight within the core.

WO 01/58741 discloses a structural reinforcement system for automobiles comprising a skeletal member and an expandable material disposed thereon for bonding the reinforcement system to the automotive frame. WO 01/68394 discloses a heat activated reinforcing sleeve comprising a polymer carrier and a heat activated structural foam reinforcing medium, such as epoxy based resin. However, these systems require complex frames having multiple reinforcing ribs.

Therefore, there remains a continued need for high performing, lightweight, cost-effective, process-friendly structural reinforcement parts for use in automobile body and body structure applications.

SUMMARY

The present invention is a structural reinforcement part for use in automobile applications, comprising:

- 1) a molded shell, having a set shape and size, comprising a polymer wall having an interior and an exterior face, wherein said interior face defines a space within the molded shell;
- 2) a structural filler material disposed in and substantially filling said space within the molded shell, and
- 3) a heat-activated expandable adhesive in contact with the exterior face of the polymer wall;

wherein the structural filler material does not undergo or require any chemical reaction or expansion, after part installation or during automotive assembly.

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Specific features and characteristics of the material components listed above can be manipulated and modified in order to provide significant design flexibility such that each part can meet its specific application performance requirements for the minimum possible part weight. The molded shell can vary in material type, shape, thickness, and number of integrated design features. The structural filler material type and density can also be varied to provide the optimum performance levels. The combined behavior of all the material comprised in the part results in superior structural performance with respect to strength, stiffness, and energy absorption characteristics.

The part components specified can be manifested into several different part embodiments. A thick-walled shell can be surrounded by lighter density foam such that the majority of the part strength is provided by the surrounding shell vessel. Another embodiment involves a thinner, semi-structural shell filled with higher density structural filler material, such that structural demands are shared by both materials. Another embodiment uses a thin-walled molded shell which functions primarily as a carrier and transfer agent for high strength and energy absorbing core filler material. Various part embodiments can also perform dual purpose as an acoustic sealer as well as a structural reinforcement.

This simplified structural reinforcement part does not require in-situ foaming of the structural filler material as in the prior art and produces a strong lightweight structural member which can be adhered to the automotive frame via the expandable adhesive, upon exposure to heat during the automotive assembly process. This structural reinforcement part offers ease of installation, since no bulk systems, pumps, or additional equipment is required.

DETAILED DESCRIPTION OF THE DRAWING

FIG. 1 is a cross-sectional view of a structural reinforcement part, wherein I is the surrounding structure of the automobile frame, II is the expandable adhesive, III is the molded shell and IV is the structural filler material.

DETAILED DESCRIPTION

The structural reinforcement part of the present invention comprises a molded shell, having a set shape and size, wherein the shell comprises a polymer wall having an interior and an exterior face, and a space defined by said interior face. The molded shell can be produced from any high temperature resistant performance plastic which can withstand process environment conditions and automotive assembly plant oven temperatures without showing significant degradation in performance. That is, the molded shell will retain its size and shape at such temperatures experienced in the automotive assembly process without any detrimental deformation. Typical plastic materials include, but are not limited to, semi-crystalline or amorphous materials including, polyamides such as nylon 6, nylon 6/6, nylon 6/6/6, polyolefins such as polyethylene or polypropylene, syndiotactic vinyl aromatic polymers such as syndiotactic polystyrene (SPS) and any blends thereof. Other potential polymers include polyesters, polyesteramides, polyarylates, polyurethanes, polyureas, polyphenylene sulfides, and polyetherimides.

The molded shell can be produced by any molding technique which will produce a shell having a set shape and size, a polymer wall having an interior and exterior face, and a space defined by the interior polymer wall face, or inner boundary of the shell. Typical molding techniques include,

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but are not limited to, well known processes such as blow molding, injection molding, rotational molding, pressure forming and the like.

The molded shell can vary in shape, size, and thickness depending on the desired cavity size and application requirements in order to balance strength, dimensional stability, and mass objectives. Preferably the molded shell is a rectangular or square shape, having a single space defined by the interior face of the shell for which to be filled with acceptable structural expandable material. Molded shell geometry can also integrate other design features such as ribs, local contours, or tack-offs in order to optimize functional part performance. Typically, the polymer wall will be a thickness so as to conserve material and reduce weight. The wall thickness will typically vary from 1.5 mm to 10 mm, depending upon the materials used and the specific application requirements.

The structural filler material can be any material which can be used to offer structural reinforcement to the molded shell. The material can be selected depending upon the properties required in the specific application.

Typically, the molded shell encases a foam structural filler material which is expanded and cured prior to part installation. The foam material is disposed in and fills the space defined within the inner face of the polymer wall. In other words the foam material is in substantial continuous contact with the inner face of the polymer wall. The foam material will typically have a density from about 5 pounds per cubic feet (80 Kg/m³) to about 25 pounds per cubic feet (400 Kg/m³) once fully expanded. The foam filler material will be injected, expanded and fully cured in the molded shell prior to installation into an automotive body cavity.

In one embodiment, the structural filler material is a polyurethane thermoset polymer foam. However, other structural filler material types can also be used such as other thermoset and thermoplastic fillers including epoxies, polyurethane hybrids, polyolefins, syndiotactics, composites, and other rigid foams. Non-plastic filler materials such as aluminum foam, organic and non-organic (ceramic and metallic) foams can also be used.

Any method of introduction into the molded shell can be used for placement of the structural filler material. Typically, filler material is placed or injected and fully-reacted within the molded shell cavity prior to insertion in the automotive body structure cavity. A pump unit, or other appropriate injection technique, can be used to inject filler material into the molded shell.

Structural filler material is typically injected into the molded shell prior to the part placement in an automotive assembly process. The molded shell will have some means of introduction, such as an insertion hole, for the structural filler material. This means can be any embodiment so as to allow for the injection or insertion of structural filler material or components thereof. Typically, components will comprise a polymer or monomers and blowing agent. In some cases the material is produced from the combination of "A-side" and "B-side" components which cure under ambient conditions. For example, the A-side may consist of isocyanate prepolymer or polymeric methylene diphenyl isocyanate (MDI) and the B-side may consist of a polyol blend nominally consisting of various polyols, surfactants, catalysts, and water. The filler material can also contain fillers such as glass beads, thixotropic additives, and other composite fibers. Blowing agents include any blowing agent which can be used with the material selected for the structural filler material and can be either chemical, physical

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blowing agents or combinations thereof. The blowing agents can be combined with the polymer in a pre-mixed state and injected into the molded shell or may be added simultaneously with the polymer or polymer components. Single component foam materials and systems can also be used, such as those described in U.S. Pat. Nos. 4,923,902 and 4,995,545, incorporated herein by reference.

In addition to the molded shell and structural filler material, the structural reinforcement part also comprises an expandable adhesive in contact with the outer face of the molded shell. The expandable adhesive can be any organic material which will activate at temperatures experienced in relevant automotive body treatment processes such as e-coat, paint, or sealer ovens, i.e. 110° C. or higher, to expand and adhere to the surrounding structure. A typical expandable adhesive includes a polymeric base material, such as an epoxy resin or ethylene-based polymer which, when compounded with appropriate ingredients (typically a blowing and curing agent), expands and cures in a reliable and predictable manner upon the application of heat. The expandable adhesive will also crosslink upon curing or achieve its final shape, rendering the material incapable of further flow or shape change. Any material that is heat-activated and expands and cures in a predictable and reliable manner under appropriate conditions, while meeting structural requirements, for the selected application can be used. Other useful materials include polyolefins, copolymers and terpolymers with at least one monomer type an alpha-olefin, phenol/formaldehyde materials, phenoxym materials, and polyurethane materials with high glass transition temperature such as in U.S. Pat. Nos. 5,766,719; 5,755,486, 5,575,525; 5,932,680 incorporated by reference.

Flowable expandable adhesive can be applied to the outer face of the shell wall in any manner, including dipping, laminating, brushing, rolling, co-extruding, and the like. Additionally, the expandable adhesive can be preformed or die-cut into pieces, which can be placed or adhered to the outer face of the shell wall. In one embodiment, the expandable adhesive is substantially continuous throughout the periphery of the outer face.

Once the reinforcement structural part is produced, the structural part can be placed in the desired cavity during automotive product assembly. Upon exposure to temperatures of 110° C. or above, the expandable adhesive on the exterior of the shell will foam and additionally adhere to the application frame, while the structural foam material will not further react or expand under such conditions. It is possible that the structural part may require some type of temporary mechanical fastener or adhesive to hold in place until the adhesive is activated. Additionally, the adhesive will expand to fill the gaps that exists between the exterior expandable material and the surrounding frame or structure.

The present invention allows for maximum flexibility with design of a structural reinforcement part due to the freedom in selection of material for both the molded shell and structural filler material. It is light in weight, and the strength of the part material can be optimized by increasing or decreasing the foam density, shell thickness, shell material type, shell design features, or overall shell geometry.

In one embodiment, the molded shell is produced from a composition comprising a nylon polymer, the structural filler is a polyurethane foam, and the expandable adhesive is an heat-activated expandable foam.

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Another aspect of the present invention is a method for producing a structural reinforcement part for automotive assembly comprising:

1) forming a molded shell, having a set shape and size, comprising a polymer wall having an interior and an exterior face, wherein said interior face defines a cavity within the molded shell;

2) injecting into said cavity a structural filler material or components thereof such that the cavity is substantially filled, and

3) contacting an expandable adhesive with the exterior face of the polymeric wall; wherein the structural filler material does not undergo or require any chemical reaction or expansion, after part installation or during automotive assembly.

What is claimed is:

1. A structural reinforcement part for use in automobile applications comprising:

1) a molded shell, having a set shape and size, comprising a polymer wall having an interior and an exterior face, wherein said interior face defines a space within the molded shell;

2) a structural filler material disposed in and substantially filling said space within the molded shell, and

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3) a heat-activated expandable adhesive in contact with the exterior face of the polymer wall, wherein the structural filler material does not undergo or require any chemical reaction or expansion, after part installation or during automotive assembly.

2. The structural reinforcement part of claim 1, wherein the molded shell is produced from a polymer selected from polyamides, polyolefins, syndiotactic vinyl aromatic polymers, and blends thereof.

3. The structural reinforcement part of claim 2, wherein the molded shell is produced from a polyamide.

4. The structural reinforcement part of claim 1, wherein the structural filler material is selected from polyurethane and aluminum foams.

5. The structural reinforcement part of claim 4, wherein the structural filler material is polyurethane foam.

6. The structural reinforcement part of claim 1, wherein the expandable adhesive is selected from expandable epoxies, polyolefins and thermoplastic polyurethanes.

7. A part according to claim 6 wherein the structural filler material has a density of about 5 to about 25 pounds per cubic foot.

* * * * *



US007132161B2

(12) **United States Patent**
Knowles et al.

(10) **Patent No.:** US 7,132,161 B2
 (45) **Date of Patent:** *Nov. 7, 2006

(54) **FIBER ADHESIVE MATERIAL**

(75) **Inventors:** Timothy R. Knowles, Del Mar, CA (US); Christopher L. Seaman, San Diego, CA (US)

(73) **Assignee:** Energy Science Laboratories, Inc., San Diego, CA (US)

(*) **Notice:** Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 107 days.

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Related U.S. Application Data

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(60) **Provisional application No. 60/390,239,** filed on Jun. 17, 2002, **provisional application No. 60/139,443,** filed on Jun. 14, 1999.

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B82B 1/00 (2006.01)
B82B 3/00 (2006.01)

(52) **U.S. Cl.** 428/364; 428/903; 428/401;
 428/376; 428/379; 977/DIG. 1; 442/330;
 442/334; 442/340; 165/185

(58) **Field of Classification Search** 385/78-80;
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 156/72, 279

See application file for complete search history.

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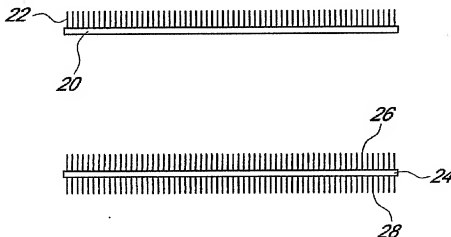
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(57)

ABSTRACT

A fiber velvet comprising nano-size fibers or nanofibrils attached to micro-size fibers is disclosed. Methods of manufacturing the velvet as well as various uses of the velvet are also described. For example, the fiber velvet can be used as a thermal interface or as an adhesive material. The nanofibrils may be attached to a flat base or membranes, or may be attached to the tip portions of the micro-size or larger diameter fibers. Various attributes of the micro-size fibers and of the nano-size fibers, for example, geometry (e.g., size, length, packing density) material type (e.g., carbon, metal, polymer, or ceramic) and properties (e.g., conductivity, modulus, surface energy, dielectric constant, surface roughness) can be selected depending on the desired attributes of the fiber velvet. The nanofibrils have a diameter of less than about 1 micron, and may advantageously be formed from single walled and/or multi-walled carbon nanotubes.

21 Claims, 9 Drawing Sheets



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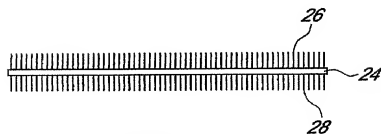
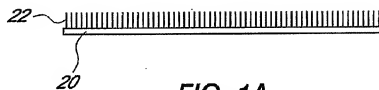
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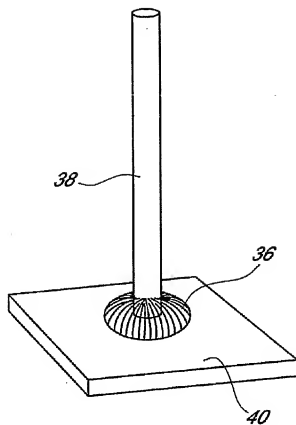


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**FIG. 2**

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FIG. 3A

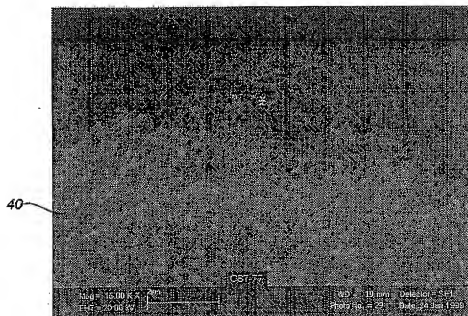
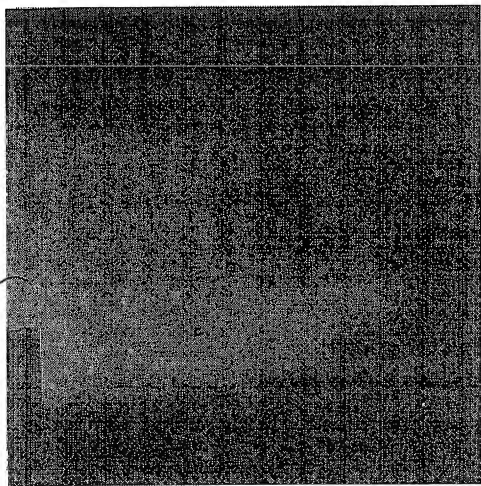


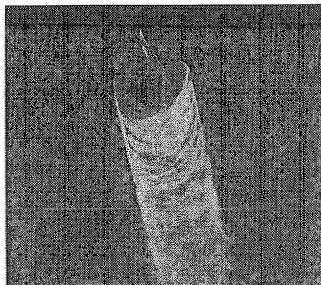
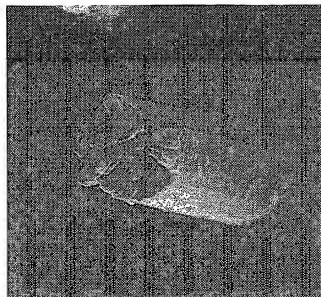
FIG. 3B

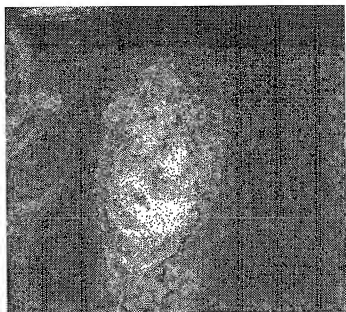
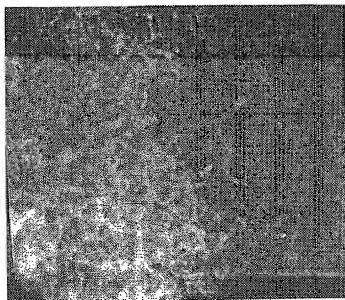
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**FIG. 4**

U.S. Patent**Nov. 7, 2006****Sheet 5 of 9****US 7,132,161 B2****FIG. 5**

U.S. Patent**Nov. 7, 2006****Sheet 6 of 9****US 7,132,161 B2****FIG. 6A****FIG. 6B**

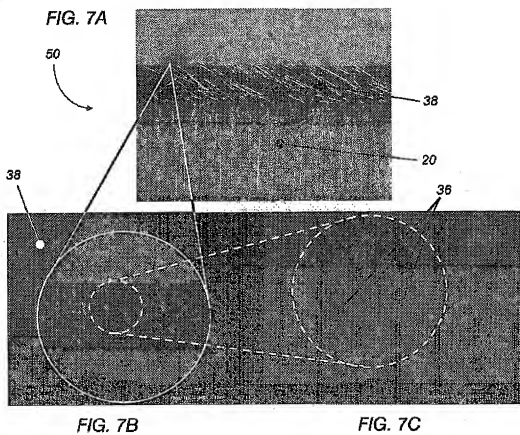
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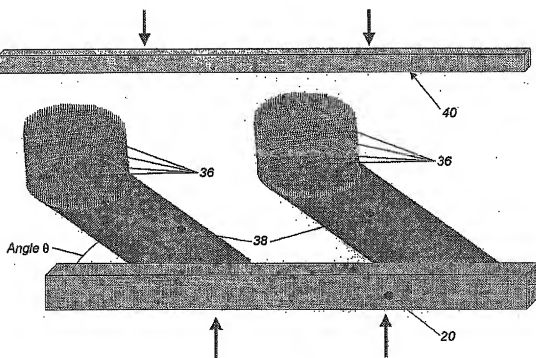


FIG. 8

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FIBER ADHESIVE MATERIAL

CROSS REFERENCE TO RELATED APPLICATIONS

This application claims priority to U.S. Provisional Patent Application Ser. No. 60/390,239, titled Dendritic Adhesive, and filed on Jun. 17, 2002 and is a continuation-in-part of U.S. patent application Ser. No. 09/593,587, titled Thermal Interface, and filed on Jun. 13, 2000, which claims priority to U.S. Provisional Patent Application Ser. No. 60/139,443, entitled Thermal Interface, and filed on Jun. 14, 1999. The entire disclosures of all of these applications are hereby incorporated by reference in their entirety.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention relates to adhesive materials such as tapes that provide a dry and reusable medium for adhering two surfaces together.

2. Description of Related Art

Much of thermal management involves the transfer of heat from one element to another. While individual elements might have very high conductance, the heat transfer rate between contact surfaces of the two elements can limit overall performance of the thermal control system. Similarly, the strength of an adhesive bond formed between the two elements is often dependent on the contacting surfaces. The heat transfer rate and adhesive strength between the two elements can improve by maximizing the contact region between the two elements.

Existing methods of bonding include brazing, soldering, gluing, bolting, taping, sewing, zippering, and use of Velcro® fasteners. Desirable properties include high strength of attachment, easy removability, reliability, and reusability. Other considerations include chemical compatibility, outgassing, and mass. Brazing and gluing with adhesive is strong, but not reusable nor easily removable. Bolts can be heavy and require special fixturing for attaching. Tape is not very strong, tends to leave a residue, and loses its sticking ability with use. It does not work well in wet environments.

A different form of adhesive is found in a foot of a Tokay gecko. The foot includes a structure which allows the gecko to run over glass ceilings or climb wet glass walls. The toes of the Tokay gecko have pads consisting of thousands of 5 um-diameter keratinous fibers (called setae). The ends of the setae split into hundreds of 100-nm-diameter fibrils. Each nanofibril terminates in an ellipsoidal structure called a "spatula." Each spatula has a diameter ranging from 200–500 nm. The adhesive force of a single seta against Si was measured to be 200 µN (20 mg). It has been hypothesized that van der Waals forces are responsible for the gecko's amazing ability to climb up smooth vertical surfaces. If utilized to full capacity, the 100 mm² area of a gecko's foot, consisting of 500,000 such setae, should then be able to produce 100 N (10 kg) of adhesive force. The corresponding effective adhesive strength is 106 MPa (15, 000 psi). This adhesive strength is well suited for many applications. The micron-size setae serve as a compliant support which conforms to the surface to allow the nanometer-sized tips (themselves compliant on a small scale) to make intimate contact with the surface.

A manufactured adhesive that could provide the adhesion properties of the gecko foot is desirable. Such an adhesive would be compliant and could stick by intermolecular (van der Waals) forces resulting from its intimate contact with the

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surface. Such an adhesive would provide broad utility as an adhesive or attachment mechanism. The adhesive could be strong, dry, removable, reusable, and lightweight, combining many of the most desirable properties of the gecko foot. Such an adhesive may also have enhanced thermal and/or electrical conductance, providing an effective thermal/electrical interface with a built-in attach mechanism that is strong, removable, and reusable.

SUMMARY OF THE INVENTION

The systems and methods of the present invention have several features, no single one of which is solely responsible for its desirable attributes. Without limiting the scope of this invention as expressed by the claims which follow, its more prominent features will now be discussed briefly. After considering this discussion, and particularly after reading the section entitled "Detailed Description" one will understand how the features of this invention provide several advantages over traditional paper coupon systems.

One aspect of the invention is an adhesive material that comprises a base, an array of first fibers bonded to the base, each having a cross sectional diameter of less than approximately 15 microns, and an array of second fibers bonded predominantly to a portion of at least some of the first fibers and having a cross sectional diameters of less than about 1 micron, the second fibers being arranged and configured to form a strong VdW bond when pressed against a mating surface.

Another aspect of the present invention is a method for making an adhesive material. The method comprises growing aligned whiskers having a diameter of less than about 1 micron from the tips of carbon fibers having a diameter of greater than about 3 microns and less than about 15 microns, and optionally depositing a material on a portion of the whiskers to form non-planar tips.

Another aspect of the present invention is an adhesive material tape that comprises a first plurality of fibers having first and second ends, the first plurality of fibers being predominantly aligned such that the first ends are bonded to a base surface of the tape, and a second plurality of fibers having first and second ends, the second plurality of fibers being predominantly aligned such that the first ends are bonded to the second ends of the first plurality of fibers and the second ends of the second plurality of fibers being arranged to adhere to a mating surface by intermolecular attraction.

Yet another aspect of the present invention is a method for enhancing the performance of an adhesive tape made from a plurality of predominantly aligned carbon fibers having diameters of less than approximately 15 microns. The method comprises placing a plurality of nanofibrils having diameters of approximately 1 micron proximate to at least some tips of the predominantly aligned carbon fibers, and depositing a film on an end portion of the nanofibrils.

Still another aspect of the present invention is an adhesive tape that comprises a central support, and a plurality of nanofibrils extending from one or both major surface(s) of the central support, wherein at least some of the nanofibrils have a diameter of less than about 1 micron, the nanofibrils being arranged and configured to form a strong vdW bond when pressed against a mating surface.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1A is a side view of one embodiment of a thermally conductive gasket incorporating nanofibrils.

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FIG. 1B is a side view of another embodiment of a thermally conductive gasket incorporating nanofibers.

FIG. 2 is a perspective view of a carbon fiber having a nanofibril attached to the tip.

FIG. 3A is a scanning electron microscope image of a 7 micron diameter fiber with a mop of nanofibrils attached to the tip.

FIG. 3B is an increased magnification of the fiber of FIG. 3A.

FIG. 4 is a scanning electron microscope image of a mop of nanofibrils which has been mechanically compressed.

FIG. 5 is a scanning electron microscope image of the tips of the fibers of a thermal gasket prior to the deposition of nanofibrils.

FIG. 6A is a scanning electron microscope image the tip of one fiber of the gasket of FIG. 5 after lapping.

FIG. 6B is a scanning electron microscope image the tip of one fiber of the gasket of FIG. 5 after lapping and carbon CVD deposition.

FIG. 6C is a scanning electron microscope image the tip of one fiber of the gasket of FIG. 5 after lapping, carbon CVD deposition, and nanofibril deposition.

FIG. 6D is a higher magnification of the nanofibril mop of FIG. 6C.

FIG. 7A is a side view of a single-sided fiber velvet that comprises an array of fibers canted at an angle.

FIG. 7B is a detailed view of one of the fibers from FIG. 7A showing nanofibrils attached to the tip of a single fiber.

FIG. 7C is a detailed view of the nanofibrils from FIG. 7B.

FIG. 8 is a perspective view of two biased carbon fibers having nanofibrils grown at an acute angle to the carbon fiber shafts.

DETAILED DESCRIPTION

Embodiments of the invention will now be described with reference to the accompanying Figures, wherein like numerals refer to like elements throughout. The terminology used in the description presented herein is not intended to be interpreted in any limited or restrictive manner, simply because it is being utilized in conjunction with a detailed description of certain specific embodiments of the invention. Furthermore, embodiments of the invention may include several novel features, no single one of which is solely responsible for its desirable attributes or which is essential to practicing the inventions herein described.

The inventions described herein relate to materials and associated devices that transfer heat between and/or adhere one device/surface and another. For example, a compliant thermal interface material developed by the applicant, which is presently marketed as VEL-THERM, is superior to existing commercial thermal interface gaskets. This material is a soft, carbon fiber velvet consisting of numerous high- κ (as high as 1000 W/mK) carbon fibers aligned perpendicularly to the interface plane. In some embodiments, such a "brush" of predominantly aligned carbon fibers is embedded in an adhesive substrate such that the tips of the fibers are attached to the surface of the substrate at one end, and are exposed at the other end. Free-standing "interleaf" gaskets can also be fabricated. These have fiber tips on both major surfaces, and the fibers are held together with an encapsulant such as a silicone or epoxy material.

Commercially available carbon fibers are formed from either pitch or PAN precursor material and drawn onto fiber tow. Each fiber typically has diameter $\sim 10 \mu\text{m}$, but which may vary between approximately 3 and 15 microns. Pitch

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fibers are graphitized by heating to high temperatures (near 3000°C.), giving them high thermal conductivities $\kappa \sim 1000 \text{ W/mK}$.

When placed between two surfaces, each fiber provides a high thermal conductivity path from one surface to the other. For uneven gaps, each fiber can bend independently in order to span the local gap. Low pressures are necessary to allow each fiber to touch both surfaces. Contact is maintained by either clamping or pressing the fiber tips into adhesive and bonding in place. By using high- κ fibers oriented in the direction of heat flow, such gaskets have a high κ (as high as 200 W/mK), while at the same time being even more compliant than conventional, particle-filled gaskets. Such velvet gaskets also work better than copper foil (at comparable pressures) because they provide a greater area of contact, conforming to uneven surfaces.

Many configurations are possible depending on the application requirements. Thus, the velvet can be bonded to one or both surfaces with various adhesives or PSA "tapes" including metal foils. The highest measured total thermal conductance has been achieved by a high- κ carbon fiber interleaf "gasket" in which the fibers are encapsulated in a silicone gel encapsulant.

The total thermal resistance of a thermal gasket interface is the sum of three contributions: the resistance of the bulk material itself, and the resistances of each interface where the material comes in contact with the interfacing surface. In terms of conductance (inverse of resistance) this may be written as:

$$h_{\text{total}}^{\text{c}} = h_{\text{bulk}}^{\text{c}} + h_{\text{interface}}^{\text{c}} + h_{\text{interface}}^{\text{c}}$$

In some embodiments, $h_{\text{bulk}}^{\text{c}} = \kappa_{\text{bulk}}/t = 400,000 \text{ W/m}^2\text{K}$, which is $40 \times$ higher than $h_{\text{metal}}^{\text{c}}$. Thus, the total joint resistance is dominated by the contact resistance between the fiber tips and the contacting surfaces. Each interface has $h_{\text{interface}}^{\text{c}} \sim 20,000 \text{ W/m}^2\text{K}$. If the contact conductance is increased to values comparable to the bulk conductance, the total conductance of the interface can be dramatically improved.

To improve this contact conductance, some embodiments of the invention utilize very small diameter fibers having diameters less than about 1 micron either in conjunction with, or as an alternative to, the typically 3–15 micron diameter conventional carbon fibers. These small diameter fibers are referred to herein as nanofibrils or whiskers. Conventional carbon and silica whiskers may be utilized. Conventional carbon whiskers may be grown from a Ni or Fe catalyst by CVD processing. However, they have typically relatively large diameters of $\sim 1 \mu\text{m}$. Furthermore, in order for conventional carbon whiskers to have high κ , they must be graphitized by heating to $\sim 3000^\circ\text{C}$.

In some advantageous embodiments of the invention, the whiskers comprise single or multi-walled carbon "nanotubes". A nanotube is a recently discovered form of carbon that is basically an elongated version of a C_{60} molecule, also known as a Buckminster Fullerene, and commonly referred to as a "Buckyball". A single-walled nanotube consists of a rolled graphene sheet, forming a tube of diameter 1.4 nm, and capped at each end. Nanotubes display many interesting and useful properties including very high thermal conductivity and high stiffness. They are highly robust; they elastically buckle, rather than fracture or plastically deform, when bent to large angles. Multiwalled nanotubes, which have larger diameters of up to about 500 nanometers, can

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also be grown, with similar properties. These properties make both single and multi-walled nanotubes surprisingly useful as components of thermal interfaces. Their thermal conductivity provides excellent heat transfer characteristics, and their mechanical properties provide the capacity to form large areas of compliant contact with adjacent surfaces.

One embodiment of a thermal interface constructed in accordance with these principles is illustrated in FIGS. 1A and 1B. Referring now to FIG. 1A, the thermal interface comprises a base 20 which has extending therefrom an array of nanofibrils 22 having diameters of less than about 1 micron. FIG. 1B illustrates a two sided nanofibril gasket. In this embodiment, the base 24 forms a central support, nanofibrils 26, 28 extend in opposite directions from both major surfaces. The central support 24 or base 20 may, for example, be about 1 to 20 or mils thick, depending on the desired mechanical properties.

Several methods of growing arrays of nanofibrils/whiskers on substrate surfaces are known in the art. Chemical vapor deposition techniques have been used to grow relatively aligned nanotubes on nickel and nickel coated glass substrates as reported in Ren, et al., *Science*, Volume 282, pages 1105-1107 (Nov. 6, 1998) and in Huang et al., *Applied Physics Letters*, Volume 73, Number 26, pages 3845-3847 (Dec. 28, 1998), the disclosures of which are hereby incorporated by reference in their entireties. Ren et al. used a plasma-enhanced chemical vapor deposition (PECVD) process in which the nanotubes grew from a nickel film catalyst in the presence of acetylene (C_2H_2), ammonia (NH_3), and nitrogen (N_2) at temperatures less than 666° C. Multiwalled nanotubes with diameters from 20-400 nm and lengths from 0.1-50 μm were obtained. Thicker Ni films resulted in larger diameter nanotubes. Transmission electron microscopy (TEM) images showed that the nanotubes were multiwalled, centrally hollow tubes, not solid fiber. Each wall is presumed to be a highly thermally conductive graphitic layer. Key to their success seems to be the introduction of ammonia, which Ren et al. conjectured participated with the nickel in the catalytic reaction. The plasma enables growth at lower temperatures. The electric field of the plasma may also play a role in forming the nanotube array.

In one advantageous embodiment, the base 20 or membrane 24 is aluminum, and the arrays of nanofibrils are created by forming a film of porous alumina on the aluminum substrate, growing nanotubes within the pores of the alumina film, and then etching away the alumina. This method is described in detail in J. Li et al., *Applied Physics Letters*, Volume 75, Number 3 (Jul. 19, 1999), the disclosure of which is hereby incorporated by reference in its entirety. With this method, a hexagonally ordered array of substantially axially aligned carbon multi-walled nanotubes on aluminum is fabricated using a hexagonal "nanochannel alumina" (NCA) membrane as a template. The template is formed on pure aluminum by anodization and consists of alumina with long, cylindrical pores with diameters from 10-500 nm diameter and lengths that span the thickness of the "membrane". Cobalt catalyst "nanoseeds" are deposited in the bottom of each pore by electrodeposition. Multi-walled nanotubes are then grown in each of the pores by hot-wall CVD at 650° C. (just below the melting point of Al). The alumina is then etched away, leaving an array of multiwalled nanotubes on an aluminum substrate. Double sided thermal gaskets as shown in FIG. 1B may be created by forming the alumina template on both sides of an aluminum sheet, and growing nanotubes on both sides. Alternatively, a thick porous alumina membrane may comprise the support.

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Outstanding features of this array are (1) uniformity of nanotube diameters, (2) near perfect alignment perpendicular to the substrate, (3) regularly spaced nanotubes in a highly ordered hexagonal lattice, (4) uniformity of nanotube lengths. Furthermore, this technique allows independent control of the nanotube diameter, length, and packing fraction. The fabrication technique has advantages over others. It eliminates the need to use a plasma, hot filament, and photolithography, involving only wet chemistry and hot-wall CVD. It can be scaled up for large areas. Furthermore, the parameters are in the proper range for application as a thermal interface, with the nanotubes being about 10-500 nanometers in diameter, a 50% packing fraction, and lengths from 1-100 microns.

In another embodiment, nanofibrils (or whiskers) are placed in contact with one or both ends of at least some of the fibers of an array of predominantly aligned larger diameter carbon fibers. In this embodiment, rather than enhancing the thermal interface performance of a foil by adding nanofibrils to one or both surfaces of a foil membrane, the performance of a carbon fiber brush/velvet which is formed from a predominantly aligned array of 3-15 micron diameter fibers is enhanced by the addition of nanofibrils to the tip region of the larger diameter fibers.

An analysis of heat transfer in the tip region of a carbon fiber gasket illustrates the importance of this region to the overall heat transfer efficiency. For small temperature differences, radiation exchange can be neglected. When the contact area is small compared to the contacting bodies, there is an extra "constriction resistance" due to bottlenecking of the heat flow through the constriction, given by:

$$R_{constriction} = 1/(4\kappa a)$$

where κ is the harmonic mean of the contacting materials: $\kappa^{-1} = \kappa_1^{-1} + \kappa_2^{-1}$, and a is the diameter of the contact area (taken to be circular). For small a , which depends on applied pressure, material hardness, tip geometry, and surface roughness, this resistance can be quite large. A conducting whisker array on the fiber tip removes the heat flow bottleneck, greatly alleviating the constriction resistance.

Attaching whiskers to the fiber tips improves thermal conductance of the gasket for several reasons. In applications where the interface is in a vacuum, the whiskers at the fiber tip will reduce the constriction resistance of the fiber contact point. In a vacuum, heat is conducted through the physical contact area between the fiber tips and the contacting surface, which is often only a small fraction of the fiber cross sectional area. The contact pressure P is low compared to the hardness H of the contacting materials ($P < 10^{-4} H$), which therefore do not deform very much. In addition, the fiber tip is not flat, being highly irregular in shape.

In the presence of air or other fluid surrounding medium, and at low contact pressures ($P < 10^{-4} H$), heat is mostly conducted through the fluid-filled gap; that is, the solid spot conduction is small compared to conduction through the fluid. Furthermore, convective heat transfer in air is usually negligible for gap widths less than ~ 6 mm. For an irregularly-shaped fiber tip, the average gap h between the bottom of the fiber and the contacting surface is of the order of the fiber radius (5 microns). Assuming conditions are such that the mean free path is small (~ 0.3 microns for air at STP) compared to h , we may use Fourier's law of heat conduction. The conductance through the bottom of the fiber is then $q/AT = \kappa b$.

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The thermal conductance through a medium of conductivity k between an isothermal flat surface and an isothermal vertical cylinder of length L and diameter D may be approximated as:

$$q/\Delta T = \frac{2\pi k L}{\ln(4L/D)}, \text{ if } D/L \ll 1.$$

We take the effective length to be about the average interfiber distance $L = D\phi^{-1/2}$, where ϕ is the fiber packing fraction. The total thermal conductance per unit area of one of the interfaces of a velvet is then approximated as:

$$h_{\text{interphase}} = \frac{2\phi k}{D} \left(1 + \frac{4L/D}{\ln(4L/D)} \right) \sim \frac{2\phi k}{D} \left(1 + \frac{4\phi^{-1/2}}{\ln(4\phi^{-1/2})} \right)$$

The second term dominates; that is, most of the heat conducts from the sides of the fiber near the tip through the conducting medium to the flat surface. For $\phi \sim 20\%$, $h_{\text{interphase}} \sim 12\phi k/D \sim 6000 \text{ W/m}^2\text{K}$ for air ($k \sim 0.025 \text{ W/mK}$) and $\sim 24,000 \text{ W/m}^2\text{K}$ for silicone encapsulant ($k \sim 0.1 \text{ W/mK}$).

Thus, a fiber tip enhanced with a nanofibril or whisker array would fill the gap with a medium with a higher effective k , thereby improving $h_{\text{interphase}}$. This may be accomplished in a variety of ways. In one embodiment, an unaligned discontinuous powder of nanofibrils is used to coat the tip region of the large fiber velvet. These powders are commercially available as, for example, type Pyrograf III whiskers from Applied Sciences, Inc. This material is a powder of cut whiskers with diameters of about 50–300 nanometers and lengths of about 20 to 80 microns. The nanofibril powder may be used as filler for thermally conductive greases, for example, which is applied to the tips of the velvet fibers. Alternatively, the powder is placed directly on the tips by soaking them in a solution of Pyrograf III in ethanol. The solution is advantageously ultrasonically vibrated to better disperse and disentangle the whiskers. After application, the presence of the nanofibrils in the tip region of the larger fibers improves heat transfer at the interface between the larger fiber tips and the surface of the component the tips are in contact with.

Because the nanofibril powder is not an aligned array of nanofibrils, there are many inter fiber interfaces which still interfere with efficient heat transfer. Thermal conductance will be improved further if the nanofibrils formed a more ordered array with the nanofibrils spanning the gap between the tip of the larger diameter fiber and the component surface from end to end. This is shown conceptually in FIG. 2. As shown in this Figure, a mop of nanofibrils 36 is attached to the tip portion of a larger diameter fiber 38. The nanofibrils 36 preferably extend predominantly away from the larger diameter fiber 38 and toward the component surface 40. In this embodiment, the nanofibrils may be configured to span the gap between each fiber and the mating surface, forming a high conductivity ($k \sim 200 \text{ W/mK}$), soft mop that effectively thermally shorts out the resistive gap. Although heat transfer efficiency between the tip of the larger fiber 38 and the component surface 40, may be expected to be better with better nanofibril alignment, even relatively poorly aligned masses of nanofibrils may be used to improve fiber tip heat transfer performance.

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In one set of gasket fabrication procedures performed by the inventors, nanofibrils were formed onto larger diameter fibers and fiber velvets. In these procedures a CVD apparatus comprising a stainless steel (SS) vacuum chamber was utilized. In this chamber, a controlled gas mixture of ammonia and hydrocarbon (propylene or acetylene) flows down through a SS tube from the top, fills the chamber, and is pumped from the bottom with a mechanical pump. The gas flow is controlled and monitored with MKS mass flow controllers. The pressure is controlled by a needle valve above the pump and monitored with a MKS Baratron gauge. A quartz window allows visual monitoring of the experiment.

The plasma is sustained between two 2"-diameter, graphite electrodes. The bottom electrode is mounted on a ceramic (mullite) tube. A SS-sheathed thermocouple runs up the inside of the tube in order to monitor the temperature of the bottom electrode. The top electrode is mounted to the SS gas inlet tube; its height can be adjusted to control the gap. The bottom electrode (anode) is grounded through the thermocouple sheath. The top electrode (cathode) is electrically isolated from the chamber and carries the (negative) high voltage, powered by a 1 kW DC power supply capable of 1000V/1A.

A hot filament is used for three purposes: (1) thermal nonequilibrium heating of the sample (2) emission of electrons to stabilize the glow discharge and prevent arcing (3) cracking of the hydrocarbon gas. Tungsten wire, 15 mil diameter, is wound into a coil and mounted between the electrodes. The support and electrical connections are made through an electrical feedthrough in the back. The filament is powered through an isolation transformer at 60 Hz. In the later CVD runs, the W coil was prevented from "drooping" when heated by supporting the coil with an alumina tube running through it, thus allowing better control of its position. Typical power applied through the coil was 200 W.

In a typical procedure, the sample, including substrate and catalyst coating, is placed on the bottom electrode. The chamber is sealed and leak tested with a He leak detector with a mass spectrometer. A gas flow of 160 sccm ammonia is established with a pressure of a few torr. An ammonia plasma is initiated between the electrodes and the tungsten filament is heated to $\sim 1500^\circ \text{C}$, as monitored by an optical pyrometer. The filament radiatively heats the sample. The temperature of the anode is monitored, although the sample is hotter than this. The sample is heated and etched for 10–15 mins. Then 80 sccm of hydrocarbon gas (propylene or acetylene) is introduced to start the CVD deposition, i.e. growth of carbon nanofibrils. After ~ 5 mins, the deposition is ceased and the chamber allowed to cool, after which the sample is removed and examined.

Dozens of PE-HF CVD runs have been performed using the techniques described by Ren et al. and Huang et al. set forth above using a number of substrates including commercially available nickel coated carbon fibers, as well as nickel coated pitch and PAN carbon fiber velvet gaskets. FIGS. 3A and 3B illustrate nanofibril "mops" 40 grown onto nickel coated 7 micron diameter carbon fibers. These nanofibrils appear to be similar in structure to commercial vapor grown carbon fibers comprising tubes of concentric, graphitic layers. However, they tend to have a high defect density, exemplified by their not being straight, and causing them to have a lower thermal conductivity than ideal. The k of these nanofibrils has not been measured, but they are most likely graphitizable, and if necessary, heat treatment at 2800°C . would likely give them a k of $\sim 2000 \text{ W/mK}$.

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Under an optical microscope, one of the "befuzzed" fibers was singled out for investigating how the nanotube mop responds to pressure exerted by a surface with which it comes into contact. The befuzzed fiber tip was contacted with flat-bladed tweezers with enough force to bend the fiber, as observed under the optical microscope. The sample was then placed in the SEM to examine the effect. Shown in FIG. 4 is an SEM image of the pressed befuzzed fiber tip. Although the diameter of the fiber is only 7 μm , the diameter of the befuzzed fiber is approximately 40 μm . Although a bit flattened, the mop can still be seen around the fiber tip, indicating some degree of mechanical resilience.

In another set of fabrication procedures, high thermal conductivity gaskets were made out of high- κ (~1000 W/mK), pitch carbon fibers (~10 micron diameter). The fibers are preferentially aligned in the z-direction such that each fiber spans the entire thickness of 1 mm. The fibers are held together with a light, epoxy wash coat. Capillary forces cause the epoxy to collect at the nodes where fibers contact each other. The packing fraction of fibers is about 10%, which implies a theoretical bulk thermal conductivity value of κ -100 W/mK and a bulk conductance of h -100,000 W/m²K.

Gaskets of a high- κ velvet (100 W/mK) attached to a POCO carbon substrate may be made by electroflocking high- κ (generally about 100-1000 W/mK) pitch fibers (for example, 10 micron diameter \times 0.5 mm length) into high- κ (~2 W/mK) carbonizable polymer such as polyimide. Electroflocking is a known technique for forming aligned fiber arrays. Pneumatic or mechanical flocking techniques may also be used. A variety of carbon fiber types may also be utilized, such as are commercially available from Amoco Corp. or Toray. A nickel film is ion beam sputtered into the velvet, most notably on the fiber tips. Carbon whisker arrays are then grown on the nickel coated fibers via PECVD processing.

The carbon fibers are precision cut from a continuous spool. Although the mean length of the pitch fibers will be controlled (typically 0.5 mm), there is some variation in length of 50 micron or more, which is comparable to the average distance between adjacent fibers. A few psi pressure is required to bend the longer fibers so that the tips of the shorter fibers contact the interfacing surface. In some embodiments, the velvet samples may be lapped and polished before deposition of the Ni film so that the fiber tips are more co-planar (within a few microns). This can be accomplished by EDM cutting or by potting the velvet in a removable medium and then lapping and polishing it flat. The potting medium is then removed.

Co-planar tips may allow the "whiskerized" velvets to have high conductivity using less than 1 psi pressure since there is no need to compress the velvet in order for all of the tips to contact the interfacing surface. Co-planar tips may also have an effect on the quality or uniformity of the whisker arrays on the tips.

In one specific process, six gaskets were potted in a removable polymer and lapped on both sides with fine sandpaper (600 grit). The potting medium was then removed. These gaskets were processed in a carbon CVD reactor in order to carbonize the epoxy wash coat and deposit a thin carbon CVD layer (~2 micron-thick) that would hold the fibers together. The resulting gaskets are then able to withstand the PE-HF CVD process. A 55 \times 5 nm-thick film of Ni catalyst was ion-beam sputtered onto both sides of four of the carbon CVD-ed gaskets.

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EXAMPLE

Pitch carbon fiber gasket sample cs7-144 was processed in the PE-HF CVD reactor under the conditions listed in Table 1

TABLE 1

PE-HF CVD deposition conditions of pitch fiber gasket sample	
Sample#	cs7-144
Mounting conditions	Lying flat on anode
Plasma power	160 W
HF power	300 W
Max temperature	527 $^{\circ}$ C.
Plasma etch time	12 min
Deposition time	5 min
Hydrocarbon gas	Acetylene
Mass gain	4.6 mg (5 %)
Resulting deposit	Heavy, bottom side

After the chamber cooled, the sample was removed and examined under the microscope. The bottom of Sample cs7-144 was covered with carbon deposit that was visible under the optical microscope. The 90.5 mg sample had gained 4.6 mg, which corresponds to a 4 micron-thick, uniform layer of carbon over one surface. Some areas displayed thicker deposits than others did. The variation may reflect variation in local temperature, hydrocarbon concentration, and/or catalyst microstructure.

FIG. 5 is a 250 \times SEM image of a pitch carbon fiber gasket, looking from above, prior to the deposit of nanofibrils to the larger diameter fibers. The preferential alignment of the fibers is evident. FIGS. 6A-6C show the tip of a single pitch fiber of Sample cs7-144 after various processing steps, FIG. 6A after lapping, FIG. 6B after carbon CVD, and FIG. 6C after PE-HF CVD. Many of the pitch fibers form a "pac-man"-shaped cross section during their manufacture. The fibers are remarkably flat after lapping. The carbon CVD deposited a uniform layer of ~2 μm of carbon, increasing the diameter of each fiber from ~12 μm to ~16 μm . It also formed a nodular structure at the tip which is no longer flat. In FIG. 6C, it is seen that the PE-HF CVD did indeed deposit an array of carbon nanofibrils on the tips and along the shafts of the fibers. FIG. 6D shows an \times 10 k view of the nanofibrils. They are not straight, but form a "mop" which appears to be highly packed. The nanofibril diameters are on the order of 100 nm.

Another means of enhancing the conductance at the tips is to add phase change material (PCM) at and around the tips. Thermally-conductive PCM is commercially available from several vendors. It is typically sold in sheet form with thicknesses from 1 to several mils. It consists of a wax (high molecular weight hydrocarbon), filled with thermally-conductive solid particles such as BN, alumina, diamond, silver flake, etc. As described above with reference to thermal grease, the phase change material may also include cut carbon nanofibrils. These particles typically have characteristic sizes from 1 to several microns. In addition, there may be wetting agents added so that the wax wets the particles, as well as the tips of the fibers.

Useful PCM is a solid at room temperature, and softens and melts at elevated temperatures. It may or may not be molten at operating temperatures. The PCM sheet is typically supported by release liner paper that is eventually peeled away before application. In some advantageous embodiments, the melting point of the material is between

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about 30 degrees C. and 100 degrees C. In some cases, the melting point is between about 40 degrees C. and 70 degree C.

The PCM can be added to the fiber tips by a number of methods. The fiber can be flocked into a sheet of PCM that is heated to just the right temperature so that the tips of the flocked fibers adhere to it and remain vertically oriented. The fibers can then be anchored to the PCM sheet by melting the PCM further and/or pushing the fiber tips further into the PCM. The resulting velvet may or may not then be partially encapsulated with silicone gel, PCM, acrylic spray, foam, or other means of encapsulation. The purpose of encapsulation is to (1) hold the fibers together, providing structural support, and (2) preventing fibers from escaping as potentially harmful debris. The latter is of special concern if the fibers are electrically conductive. Next, a PCM sheet can be placed on top of the resulting velvet, and the entire PCM/velvet/PCM sandwich pressed together and/or heated to fuse everything together.

This material has several advantages over the use of thermal grease and elastomer potted velvets. Similar to grease, high thermal conductivity PCM improves interface conductance. However, the PCM may be localized preferentially near the tips. This makes gasket very compliant, unlike velvet that is totally filled with elastomer. Furthermore, solid PCM is not messy at room temperature like thermal grease, it supports velvet at room temperature when in solid form, and PCM acts as an adhesive that prevents fibers from escaping as debris.

Adhesive Material

The nanofiber material described above, which may advantageously include coupling nanofibrils to the larger fibers to form a fiber velvet, can also be used as an adhesive material. As explained above, fiber velvets can form compliant interface pads. These pads can be effective as a thermal interface since they make contact at their fiber tips. For uneven gaps, most or all of the fibers can bend independently in order to span the local gap. Low pressures are sufficient to allow substantially all of the fibers to touch both surfaces. These same attributes are also desirable in an adhesive. An adhesive material that incorporates a fiber velvet provides a dry and reusable medium for adhering to a mating surface.

FIG. 7A is a perspective view of a single-sided fiber velvet 50 that comprises an array of fibers. FIG. 7B is a detailed conceptual view of one of the fibers from FIG. 7A showing an array of nanofibrils 36 attached to the tip of a single fiber 38. The end of the fiber 38 that is distal to the nanofibrils 36 is fixedly attached to a base or substrate material 20 using one of the methods described above. The ends of the nanofibrils 36 that are distal to the fiber 38 are available for adhering to a mating surface.

Many configurations are possible depending on the application requirements. Thus, the fibers can be bonded to one or both surfaces of a central support with various adhesives or pressure sensitive adhesive (PSA) "tapes" including metal foils and polymers. A single-sided velvet 50 shown in FIG. 7A forms a flexible one-sided tape. Alternatively, a second array of fibers may be attached to a lower surface of the base 20 to form a two-sided tape. Previously described exemplary materials for the substrate or base 20 include a POCO graphite substrate a foil of aluminum, or a plastic film.

The fibers 38 can be, for example, any commercially available type. Commercially available carbon fiber include those formed from either pitch or PAN precursor material and drawn onto fiber tow. The carbon fibers 38 may be precision cut from a continuous spool.

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The term "fiber" as used herein refers to a structure with greater than a 1:1 aspect ratio. The terms "nanofiber" or "nanofibril" as used herein refers to a fiber with a diameter of equal to or less than about 1 μm (micrometer).

Each fiber typically has a diameter of 6–10 μm , but which may vary between approximately 3 and 15 microns. In some embodiments, the fibers 38 of the carbon fiber velvet 50 have diameters that range from approximately 5 μm to 10 μm with lengths that range from approximately $\frac{1}{2}$ mm to 3 mm. Electroflocking can be used to form the aligned fiber arrays 38 on the base 20. Pneumatic or mechanical flocking techniques may also be used.

Depending on the desired attachment scheme between the fiber velvet 50 and the mating surface, various geometric and material attributes of the fibers 38 can be selected. These attributes include material properties of the fibers and substrate, for example adhesive strength, modulus, Hamaker constant, dielectric constant, surface energy, and tensile strength and modulus and temperature regimes. These attributes also include geometry, for example, fiber length, fiber diameter, fiber number density, fiber angular bias, and pad thickness. For example, the diameters and lengths of the fibers 38 can be selected depending on the desired compliance of the adhesive material produced with them. To create a more compliant adhesive, fibers with a smaller diameter, longer length, or smaller modulus can be selected.

Once the material and diameter are selected, the fibers 38 can be precision cut to the desired length and assembled into the velvet using the techniques described above. For one embodiment in an adhesive application, 6- μm diameter \times 1.5-mm long ex-polyacrylonitrile (ex-PAN) carbon fibers are selected for the carbon fibers 38. These ex-PAN fibers are a glassy carbon and have the advantages of a small diameter, are easy to bend, bend elastically, and do not break easily.

The fiber density of the fibers 38 also affects the properties of the adhesive material. Fiber density is the density of the fibers 38 in the fiber velvet 50. Fiber density is also referred to as a packing fraction. Thus, the packing fraction selected may also be based on the desired properties of the carbon fiber velvet 50. For example, a high (20%) packing fraction could be used if relatively low compliance but high adhesive strength was desired. However, for an adhesive application, the packing fraction can be selected as low as a few percent. A lower packing fraction increases the compliance of the resulting carbon fiber velvet 50.

To substantially improve the adhesive strength of the carbon fiber velvet 50 with a mating surface, arrays of carbon nanotubes/whiskers/nanofibrils 36 are deposited onto or grown from the tips of the carbon fibers 38. The deposited nanofibrils 36 can be arranged in a "mop" or in an aligned configuration on the tips of the carbon fibers 38. The aligned configuration has similarities to the contact ends of the setae of the gecko foot and is illustrated in FIGS. 7B and 7C. As with the fibers 38, the characteristics or attributes of the nanofibrils 36, for example, diameter, length, packing fraction, location, as well as their properties, for example, thermal and mechanical, can vary. Many of the characteristics of the nanofibrils 36 can be controlled by the growth process and tailored to match or surpass that of the split nanofibrils at the end of a Gecko's seta.

An exemplary process for growing nanofibrils 36 on a substrate will now be described. In this process, a thin film of nickel or cobalt catalyst was deposited onto the substrate by ion-beam sputtering. The substrate can be ion-beam cleaned prior to deposition. The resulting film thickness was monitored with a quartz crystal thickness monitor and varied from 1–13 nm thick. Thinner films promote growth of

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smaller diameter nanofibrils 36. An optional step in the process for growing nanofibrils 36 comprises the deposition of a buffer layer between the substrate and the thin film prior to catalyst deposition. The addition of the buffer layer may promote formation of Ni nanodots upon heating. The inclusion of a buffer layer may facilitate bonding of the nanofibrils 36 to the substrate. For example, a titanium (Ti) buffer layer can form a TiC "weld" between the nanofibrils 36 and the substrate.

The nanofibrils 36 were grown on the substrate in a PECVD reactor. The PECVD included a 1200° C. tube furnace with a 3"-diameter quartz tube. Cylindrical graphite electrodes were machined and assembled within the PECVD reactor. The substrate and deposited catalyst was placed on a lower electrode. The quartz tube was evacuated to less than 10 mtorr with a mechanical pump, and continued pumping as the temperature was raised to 700 or 750° C. Once the setpoint temperature was reached, an etchant gas (NH₃) was fed at a controlled rate (typically 200 sccm/min) with the pressure being adjusted to a few torr. High voltage (typically 600 V) was then applied between the electrodes and a plasma was initiated. Optionally, the NH₃ plasma is allowed to etch the substrate and deposited catalyst for several minutes before starting nanofibril 36 growth. The heating and/or etching step is critical in breaking up the catalyst film on the substrate to form nanodot seeds. Etching reduces the size of the nanodot seeds and breaks up larger nanodot seeds into smaller nanodot seeds. The size and density of the nanodot seeds determine the diameter and density of the nanofibrils that subsequently grow from the nanodot seeds. On silicon substrates, the diameter and density of the nanofibrils correlate with the Ni film thickness.

A controlled flow of feed gas, for example acetylene, is then fed to initiate nanofibril growth. Details of the Ni-substrate interaction determine whether and how the nanodots form. Depending on the adhesion between the Ni catalyst and the substrate, the nanofibrils 36 may grow in base-growth or tip-growth modes. Base-growth mode occurs when the catalyst seed remains attached to the substrate and the nanofibril grows out of the catalyst seed. Tip-growth mode occurs when the catalyst seed is carried with the tip of the nanofibril as the nanofibril grows from the catalyst seed. Adhesion of the Ni catalyst to the substrate promotes base growth. After about 15 minutes, the plasma was turned off and the gas flow stopped. The substrate and grown nanofibrils were allowed to cool in vacuum.

Other methods for growing well-aligned nanofibrils on a substrate are described in U.S. Pat. No. 6,361,861 to Gao et al., which is hereby incorporated by reference in its entirety and by Li et al., Appl. Phys. Lett. 75, 367 (1999).

The attributes of an exemplary fiber velvet 50 that comprises arrays of nanofibrils 36 attached to carbon fibers 38 are described below. A combined packing fraction for the velvet 50 is calculated by multiplying the packing fraction of the carbon fibers 38 with the packing fraction of the nanofibrils 36. The combined packing fraction for the exemplary velvet 50 described below is 2% (10% carbon fibers; 20% nanofibrils).

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-continued

Carbon Nanotube (CNT) array on a carbon fiber tip	
Aspect ratio, $\alpha = L/D$	100-200
Packing fraction, ϕ	10%
Young's modulus, E	234 GPa
Rad Compliance ($E\phi/\alpha^2$)	$\sim 10^6$ Pa
Multi-Walled Nanotube (MWNT) array 36	
Diameter, D	20-200 nm
Length, L	10-50 μ m
Aspect ratio, $\alpha = L/D$	1000
Packing fraction, ϕ	20%
Young's modulus, E	1000 GPa (est)
Rad Compliance ($E\phi/\alpha^2$)	$\sim 10^5$ Pa

As explained with reference to FIGS. 6A-6C, the carbon fibers 38 can be lapped and polished to form a carbon fiber velvet 50 with a uniform length and flat tips. Lapping and polishing before attaching or growing nanofibrils 36 results in the fiber tips being more co-planar (within a few microns). This geometry provides a flat surface from where to grow the nanofibrils or nanotubes 36. Such controlled tip geometry enhances the consistency of the adhesive surface of the nanotubes or nanofibrils 36 that grow on the flat tips of the carbon fibers 38. One method of lapping the fiber tips involves potting the fibers 38 during lapping of the carbon fiber tips. After lapping, the potting medium is removed from between the carbon fibers 38. An example of such a removable potting medium is mothballs. However, lapping and polishing of the carbon fiber tips is not required for the subsequent attachment of the nanofibrils 36 thereon. Alternatively, electro-discharge machining (EDM) can be used to flatten the ends of the carbon fibers 38 prior to attachment of the nanofibrils 36.

FIG. 8 illustrates a single fiber 38 that is at a bias angle θ with respect to the base material 20. A biased velvet has fibers 38 which are not perpendicular to the underlying base 20. Embodiments of the velvet include fibers 38 that are biased in the same direction with respect to the base 20. Angles between 0 and 90 degrees can be selected. Biasing the carbon fibers 38 can further increase the compliance of the carbon fiber velvet 50. In one embodiment of the carbon fiber velvet 50, an angle of about 45 degrees is formed between the underlying base 20 and the carbon fibers 38.

By biasing the carbon fibers 38 at a particular angle and then lapping the tips of the carbon fibers 38, the nanofibrils 36 can be grown or attached at a particular angle to the carbon fiber 38 shafts as shown in FIG. 8. For example, as illustrated in FIG. 8, the nanofibrils can be grown or attached at an angle that is complementary to the angle θ so that the nanofibrils 36 are normal to the base 20 and/or a mating surface 40. Alternatively, the nanofibrils 36 are grown or attached at an angle with respect to the carbon fiber shafts so that the nanofibrils 36 are not perpendicular or normal to the base 20 and/or the mating surface 40. These angled nanofibrils 36 with respect to the carbon fiber shafts may be more compliant than the carbon fibers 38 when contacting the mating surface 40.

Any of the deposition techniques previously described, including CVD, PECVD, or using an AO template, can be used to grow carbon nanofibrils 36 on the tips of carbon fibers 38. These deposition techniques utilize a nano-sized metal catalyst (e.g., nickel, iron, or cobalt) particle on the carbon fiber 38 tip from which the carbon nanotubes grow. The catalyst might remain to provide a strong bond to the

Carbon Nanotube (CNT) array
on a carbon fiber tip

Carbon fiber 38

Diameter, D 5 μ m
Length, L 500-1000 μ m

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carbon fiber 38 tip. The strength of the base attachment can be improved by, for example, heat treatment. Another means by which the nanofibril can remain strongly attached to the fiber tip is by reacting the carbon nanofibril with a layer of Ti or other metal to form TiC or other appropriate carbide as a weld. Still another method of strongly attaching the carbon nanofibrils to the carbon fiber tip is by encapsulating with a conformal coating of carbon by chemical vapor deposition (CVD).

One method of depositing the catalyst particles on the ends of the carbon fibers 38, is by ion beam sputtering a thin film of catalyst metal onto the carbon fiber 38 tips, and then appropriate heat treatment and/or etching in order to create nanometer-sized catalyst particles. The nanofibril 36 arrays then grow on the catalyst coated fibers 38 via PECVD processing. In embodiments where the nanofibrils 36 are grown at ~650 degrees C., a carbonizable adhesive can be used to attach the carbon fibers 38 to a carbon (e.g. POCO graphite) substrate. Such a configuration for the carbon fibers 38 and nanofibrils 36 results in comparable size, length, and packing fraction values to that of Tokay gecko setae.

The nanotubes 36 can be coated for specific environments. For example, coating the nanotubes with SiC enhances their high temperature capability in an oxidizing atmosphere (such as air).

The diameter of the nanofibrils 36 affects the adhesive strength between the tips of the nanofibrils 36 and the mating surface 40. It is postulated that once intimate contact between the nanofibrils 36 of the adhesive material and the mating surface 40 occurs, the compliance of the nanofibrils 36 allows the adhesive material to stick to the mating surface 40 by intermolecular (van der Waals) forces. The van der Waals (vdW) force occurs between the uncharged atoms of the mating surface 40 and the uncharged atoms of the nanofibrils 36. These vdW forces occur due to the mutual induction of an electric dipole moment in each atom. These mutually-induced electrical dipoles attract the nanofibril 36 to the mating surface 40 and vice versa. To maximize the vdW adhesion, it is desirable that the nanotubes 36 be relatively straight or slightly curved, have high packing fraction, small, uniform diameters, and long, uniform lengths.

The dipole-dipole pair potential for the vdW forces is given by $V = -C/d^6$, where C is a constant roughly proportional to the polarizabilities of the atoms. The vdW force between macroscopic bodies is the sum of all forces between atoms of one body and those of the other. While the vdW force is usually thought to be small between two atoms, it can be quite large between macroscopic bodies, especially when in close contact.

The vdW force between a sphere of radius R and a flat surface, separated by distance D is:

$$F = \frac{AR}{6D^3}$$

where A is the Hamaker constant defined as $A = \pi C \rho_1 \rho_2$, ρ_1 and ρ_2 are the number of atoms per volume in the two bodies, and C is the coefficient in the atom-atom pair potential $V = -C/d^6$. Because C is roughly proportional to the polarizabilities of the two materials, A is approximately constant (i.e. independent of density) for all materials, lying in the range $0.3\text{--}6 \times 10^{-19}$ J for solid bodies. For further discussion see Israelachvili, J. N., *Intermolecular and Sur-*

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face Forces, published by Academic Press, San Diego, 1985 which is hereby incorporated by reference in its entirety.

The adhesive pressure over the projected area of the sphere is therefore:

$$P = \frac{F}{\pi R^2} = \frac{A}{6\pi D^3 R}$$

For an array of spheres with packing fraction ϕ , the adhesive force per area becomes:

$$P = \frac{A\phi}{6\pi D^3 R}$$

Taking $A = 10^{-19}$ J, $D = 0.3$ nm, and $\phi = 6\%$, the calculated adhesive strength for spheres, or fibers with hemispherical tips, as a function of sphere/fiber radius are listed below.

Fiber radius, R	Force per fiber, F (N)	P (psi)
2 microns	3.70E-07	0.26
200 nm	3.70E-08	2.6
20 nm	3.70E-09	26
2 nm	3.70E-10	260

This model shows that more smaller fibers adhere more strongly than fewer large fibers of equal area because more atoms are in closer contact with the flat mating surface 40. Furthermore, as the fiber radius reaches the nanometer range as with nanofibrils 36, the adhesive strength can reach hundreds of psi.

The density or packing fraction of the nanofibrils 36 affects the adhesive strength between the tips of the nanofibrils 36 and the mating surface 40. While the gecko foot has of the order 10^6 nanofibrils per mm^2 , the nanotube arrays 36 have typical densities of $10^7\text{--}10^9/\text{mm}^2$ as described in Ren et al. and Li et al. For a carbon fiber 38 packing fraction of 10%, this would give a nanofibril 36 density of $10^6\text{--}10^7$, which is comparable to or higher than the density for the gecko foot.

The aspect ratio of the nanofibrils 36 can be selected such that they will be able to bend and conform to any contacting mating surface 40. In one embodiment, a nanotube array 36 with 50 nm diameter \times 5 μm length would include such attributes.

Depositing additional material on the contact surface of the nanofibrils 36 can further enhance their adhesive strength to the mating surface 40. For example, if the nanofibrils 36 are open at the ends and have insufficient tip area for high adhesive strength, the nanofibril 36 tips can be encapsulated or filled. This filling can be accomplished by, for example, depositing a thin film with a thickness that is comparable to the nanofibril 36 diameter. The encapsulating material could be, for example, a metal or a compliant polymer such as parylene. The encapsulating material can comprise, for example, conductive particles. The electrical characteristics of these conductive particles can be varied depending on the attributes desired of the adhesive material.

For line of sight deposition on the tips of the nanofibrils 36 by sputtering or evaporation, the deposited thin film can be thickest at the tips and thinned out on the upper surface area of the nanofibrils 36. Such an enhanced tip of the nanofibril 36 serves a similar purpose as a gecko spatula to

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the setae. If a non-planar or rounded geometry is attained for the tip of the nanofibril 36, such a rounded tip may adhere well in various orientations.

Depending on the microstructure of the carbon fiber velvet 50, the microstructure may be susceptible to clogging by dirt or other particles. The attributes of the microfibrils 36 can be further selected to enhance self-cleaning whereby the contaminants are expelled from the microstructure. For example, it may be important for the material to be hydrophobic to enable this self-cleaning feature, and or comprise a certain packing fraction of nanofibrils. These features are used by the lotus plant to keep it clean. In this way, the attributes of the fibers can be optimized to reduce the effect of contaminants on the adhesive properties of the material.

One of the advantages of this nanostructure is that the adhesive material is compliant and therefore able to conform to both flat and nonflat or rough surfaces with a minimal amount of applied pressure. Another advantage is that the adhesive material makes dry contact, sticking by intermolecular (van der Waals) forces, without leaving a sticky residue. Other advantages include: controlled design and manufacture, enabling tailoring and optimizing of array features by modifying fiber and nanotube diameters, lengths, packing fractions, orientation, and location.

Exemplary applications of the adhesive material described herein include a wide range of ambient, and even hostile conditions: submarine, high temperature, space vacuum, and chemically corrosive environments. In some advantageous embodiments of the invention, the thermal conductivity and/or electrical conductivity of the carbon fibers can be combined with the adhesive properties. This can produce an electrical or thermal gasket/interface material that sticks without glue or mechanical fasteners to the components it is in contact with.

The foregoing description details certain embodiments of the invention. It will be appreciated, however, that no matter how detailed the foregoing appears in text, the invention can be practiced in many ways. As is also stated above, it should be noted that the use of particular terminology when describing certain features or aspects of the invention should not be taken to imply that the terminology is being re-defined herein to be restricted to including any specific characteristics of the features or aspects of the invention with which that terminology is associated. The scope of the invention should therefore be construed in accordance with the appended claims and any equivalents thereof.

What is claimed is:

1. An adhesive material for attaching to a mating surface, comprising:
 - a base;
 - an array of electroflocked first fibers bonded to the base, each having a cross sectional diameter of less than approximately 15 microns; and
 - an array of second fibers bonded predominantly to a distal portion of at least some of said first fibers and having a cross sectional diameters of less than about 1 micron, said second fibers being arranged and configured to

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form an intermolecular (e.g. van der Waals) bond when pressed against the mating surface.

2. The adhesive material of claim 1, wherein the first fibers have a diameter of approximately 5 to 10 microns.
3. The adhesive material of claim 1, wherein the second fibers have a diameter of approximately 0.005 to 0.5 microns.
4. The adhesive material of claim 1, wherein the second fibers are substantially parallel to the first fibers.
5. The adhesive material of claim 1, wherein the first fiber extends in a normal direction from the base.
6. The adhesive material of claim 1, wherein the first fiber extends in a direction to form an oblique angle with the base.
7. The adhesive material of claim 6, wherein the second fibers are substantially skew to the first fiber.
8. The adhesive material of claim 7, wherein the second fibers are substantially parallel to a normal direction extending from the base.
9. The adhesive material of claim 1, wherein the second fibers comprise carbon nanotubes.
10. The adhesive material of claim 1, wherein the first fiber extends from at least one side of the base.
11. The adhesive material of claim 10, wherein the first fiber extends from both sides of the base.
12. The adhesive material of claim 1, further comprising a coating material located on tips of the second fibers and in contact with the first surface.
13. The adhesive material of claim 12, wherein the coating material is a metal.
14. The adhesive material of claim 12, wherein the coating material is a polymer.
15. The adhesive material of claim 1, wherein the portion is the fiber tip area.
16. The adhesive material of claim 1, wherein the first fiber and the second fibers both comprise carbon.
17. The adhesive material of claim 1, wherein an adhesive force between the adhesive material and the mating surface is approximately equal to or greater than 0.26 psi.
18. The adhesive material of claim 1, wherein an adhesive force between the adhesive material and the mating surface is approximately equal to or greater than 2.6 psi.
19. The adhesive material of claim 1, wherein an adhesive force between the adhesive material and the mating surface is approximately equal to or greater than 26 psi.
20. The adhesive material of claim 1, wherein an adhesive force between the adhesive material and the mating surface is approximately equal to or greater than 260 psi.
21. A fabricated microstructure, comprising:
 - a base;
 - a shaft with a length of about 500 microns and being connected to the base, said shaft having a diameter of between about 3 and 15 microns; and
 - an array of whiskers having terminal ends formed at an end of said shaft distal from said base, said array of whiskers having a width of less than about 10 microns.

* * * * *



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(12) **United States Patent**
Uitenbroek et al.

(10) **Patent No.:** **US 6,982,231 B1**
 (45) **Date of Patent:** **Jan. 3, 2006**

(54) **ELASTOMERIC, BREATHABLE LAMINATE
 WITH ENHANCED BREATHABILITY UPON
 EXTENSION**

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 264/291

(58) **Field of Classification Search** 442/77,
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 264/288.8, 290.5, 291

See application file for complete search history.

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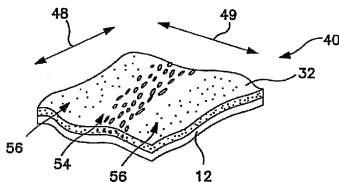
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(57) **ABSTRACT**

An elastomeric, breathable laminate having enhanced
 breathability is formed by bonding a breathable,
 microporous, extendible/elastic film to a nonwoven facing
 material. The facing material can be necked to impart
 cross-directional stretchability. Once the film and the facing
 material are bonded together, the resulting laminate is
 stretched in one or more areas to impart higher breathability
 to selected areas of the laminate. The breathable laminate
 with enhanced breathability is particularly useful as an outer
 cover for diapers and other personal care products.

32 Claims, 5 Drawing Sheets



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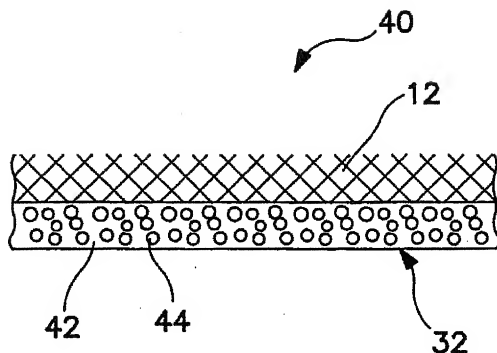


FIG. 1

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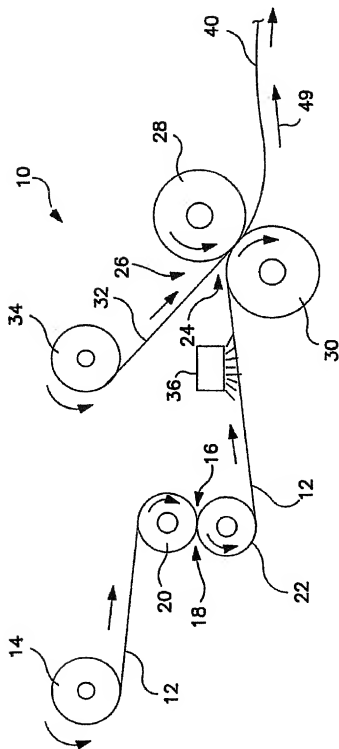


FIG. 2

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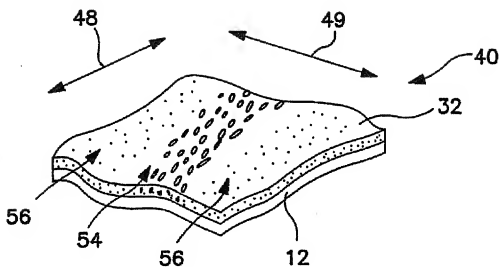


FIG. 4

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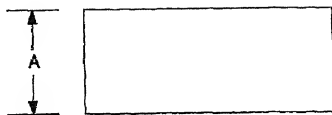


FIG. 5

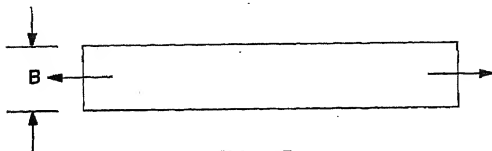


FIG. 6

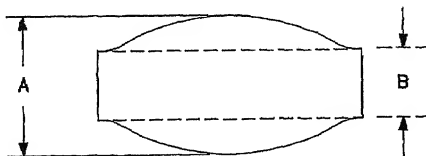


FIG. 7

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ELASTOMERIC, BREATHABLE LAMINATE WITH ENHANCED BREATHABILITY UPON EXTENSION

FIELD OF THE INVENTION

This invention is directed to a breathable laminate configured to selectively enhance breathability in target areas.

BACKGROUND OF THE INVENTION

Breathable materials, such as breathable films, typically block the passage of particulate matter, water and other liquids while allowing water vapor and air to pass through the material. Thus, breathable materials are particularly suitable for use in garments and personal care products, thereby allowing moisture trapped beneath the fabric to escape as water vapor. Garments using breathable materials are generally more comfortable to wear since the migration of water vapor through the fabric helps to reduce and/or eliminate discomfort resulting from excess moisture trapped against the skin. Furthermore, the reduction of excess moisture leads to reduced relative humidity and temperature within the garment in comparison to such garments made of non-breathable films and laminates.

One example of a breathable material is a microporous film. This type of film is typically filled with particles or other matter and then crushed or stretched to form a fine pore network of micropores of a size and/or frequency to impart the desired level of breathability to the fabric. The microporous film can be laminated to a nonwoven web to create a laminate that takes advantage of the strength and integrity of the nonwoven web and the barrier properties of the stretched film. One example of such a laminate is disclosed in U.S. Pat. No. 6,045,900 issued to Haffner, et al.

Breathable laminates, including a layer of breathable film and one or more layers of other materials, are often not breathable enough, thereby resulting in excess vapor retention within the garment, personal care product, or other application made of the breathable laminate. In diapers and other pant-like absorbent articles, liquid can accumulate in the crotch region. When this happens, heat from the wearer's body can cause the space between garment and the wearer to become saturated with water vapor, facilitating the occurrence of diaper rashes and other skin irritations. The most effective way to vent the water vapor is through other regions of the garment which are not affected by the pool of liquid in the crotch.

There is a need or desire for a breathable laminate having enhanced breathability.

SUMMARY OF THE INVENTION

The present invention is directed to a microporous, extensible/elastic material having enhanced breathability. More particularly, the breathability of the material is increased in target zones of the material. The material is a laminate formed from a breathable, elastic, microporous film laminated to a nonwoven facing material. The nonwoven facing material can be necked to impart cross directional stretch. Target zones of higher breathability can be created by stretching the laminate in the target areas. The laminate is particularly useful as an outer cover for diapers and other personal care products.

The film can be a microporous film made of any elastomeric polymer. Suitable films can deliver breathability, expressed as water vapor transmission rate (WVTR), in a

range of about 1,000 to 30,000 grams/m²-24 hours using the Mocon WVTR test procedure described below. The targeted zones of high breathability can have a WVTR at least 10% greater than the remainder of the material. Suitable films include microporous films which contain an amorphous polymer and a filler.

The necked nonwoven facing material is extensible at least in the cross direction. Cross direction stretchability is achieved through necking the nonwoven material in the machine direction. Materials having machine direction stretchability can be used to impart machine direction stretchability to the resulting laminate. The film and the nonwoven facing material can be adhesively bonded together.

With the foregoing in mind, it is a feature and advantage of the invention to provide a breathable laminate having targeted zones of high breathability;

It is also a feature and advantage of the invention to provide an improved breathable laminate useful in a wide variety of diaper outer covers, other personal care products, surgical gowns, and other breathable applications.

The foregoing and other features and advantages of the invention will become further apparent from the following detailed description of the presently preferred embodiments, read in conjunction with the examples and drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross-sectional view of a breathable laminate of the present invention;

FIG. 2 is a schematic representation of an exemplary process for forming a composite breathable laminate with enhanced breathability;

FIG. 3 is another schematic of an exemplary process for forming a composite breathable laminate with enhanced breathability;

FIG. 4 is a perspective view of a breathable laminate of the present invention;

FIG. 5 is a representative plan view of an exemplary facing material before tensioning and necking;

FIG. 6 is a plan view of an exemplary facing material necked in a machine direction; and

FIG. 7 is a plan view of an exemplary composite material while partially stretched in the cross direction.

Definitions

Within the context of this specification, each term or phrase below will include the following meaning or meanings.

"Bonded" refers to the joining, adhering, connecting, attaching, or the like, of two elements. Two elements will be considered to be bonded together when they are bonded directly to one another or indirectly to one another, such as when each is directly bonded to intermediate elements.

"Cross direction" refers to the width of a fabric in a direction generally perpendicular to the direction in which it is produced, as opposed to "machine direction" which refers to the length of a fabric in the direction in which it is produced.

"Cycle" and "cycling" refer to a process of repeatedly stretching and retracting a material to either test material properties or to activate latent material properties.

"Elastic," "elastized" and "elasticity" mean that property of a material or composite by virtue of which it tends to recover its original size and shape after removal of a force causing a deformation.

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"Elastomeric" refers to a material or composite which can be elongated by at least 50 percent of its relaxed length and which will recover, upon release of the applied force, at least 40 percent of its elongation. It is generally preferred that the elastomeric material or composite be capable of being elongated by at least 100 percent, more preferably by at least 500 percent, of its relaxed length and recover, upon release of an applied force, at least 50 percent of its elongation.

"Film" refers to a thermoplastic film made using a film extrusion and/or foaming process, such as a cast film or blown film extrusion process. For the purposes of the present invention, the term includes breathable microporous films that act as liquid barriers.

"Layer" when used in the singular can have the dual meaning of a single element or a plurality of elements.

"Liquid permeable material" or "liquid water-permeable material" refers to a material present in one or more layers, such as a film, nonwoven fabric, or open-celled foam, which is porous, and which is permeable to the flow of water and other aqueous liquids through the pores or openings. The pores or openings in the film or foam, or spaces between fibers or filaments in a nonwoven web, are large enough and frequent enough to permit leakage and flow of liquid water through the material.

"Machine direction" refers to the length of a fabric in the direction in which it is produced, as opposed to "cross direction" which refers to the width of a fabric in a direction generally perpendicular to the machine direction.

"Meltblown fiber" means fibers formed by extruding a molten thermoplastic material through a plurality of fine, usually circular, die capillaries as molten threads or filaments into converging high velocity heated gas (e.g., air) streams which attenuate the filaments of molten thermoplastic material to reduce their diameter, which may be to microfiber diameter. Thereafter the meltblown fibers carried by the high velocity gas stream are deposited on a collecting surface to form a web of randomly dispersed meltblown fibers. Such a process is disclosed for example, in U.S. Pat. No. 3,849,241 to Butin et al. Meltblown fibers are microfibers which may be continuous or discontinuous, are generally smaller than about 0.6 denier, and are generally self bonding when deposited onto a collecting surface. Meltblown fibers used in the present invention are preferably substantially continuous in length.

"Nonwoven" and "nonwoven web" refer to fibrous materials and webs of fibrous material which are formed without the aid of a textile weaving or knitting process.

"Polymers" include, but are not limited to, homopolymers, copolymers, such as for example, block, graft, random and alternating copolymers, terpolymers, etc. and blends and modifications thereof. Furthermore, unless otherwise specifically limited, the term "polymer" shall include all possible geometrical configurations of the molecules. These configurations include, but are not limited to isotactic, syndiotactic and atactic symmetries.

"Selectively stretched" refers to stretching certain regions of a material to a greater extent than other regions of the material. The selection of the regions to be stretched to a greater extent can be strategically planned based on a desired level of breathability in those regions of the material, with the regions stretched to a greater extent having higher breathability than the regions stretched to a lesser extent.

"Spunbonded fiber" refers to small diameter fibers which are formed by extruding molten thermoplastic material as filaments from a plurality of fine capillaries of a spinnerette having a circular or other configuration, with the diameter of the extruded filaments then being rapidly reduced as

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described, for example, in U.S. Pat. No. 4,340,563 to Appel et al., and U.S. Pat. No. 3,692,618 to Dorschner et al., U.S. Pat. No. 3,802,817 to Matsuki et al., U.S. Pat. Nos. 3,338, 992 and 3,341,394 to Kinney, U.S. Pat. No. 3,502,763 to Hartmann, U.S. Pat. No. 3,502,538 to Petersen, and U.S. Pat. No. 3,542,615 to Dobo et al., each of which is incorporated herein in its entirety by reference. Spunbond fibers are quenched and generally are not tacky when they are deposited onto a collecting surface. Spunbond fibers are generally continuous and often have average deniers larger than about 0.3, more particularly, between about 0.6 and 1.0.

"Stretchable" means that a material can be stretched, without breaking, by at least 50% (to at least 150% of its initial unstretched length) in at least one direction, suitably by at least 100% (to at least 200% of its initial length), desirably by at least 150% (to at least 250% of its initial length). The term includes elastic materials as well as materials that stretch but do not significantly retract.

"Superabsorbent" or "superabsorbent material" refers to a water-swelling, water-insoluble organic or inorganic material capable, under the most favorable conditions, of absorbing at least about 15 times its weight and, more desirably, at least about 30 times its weight of an aqueous solution containing 0.9 weight percent sodium chloride. The superabsorbent materials can be natural, synthetic and modified natural polymers and materials. In addition, the superabsorbent materials can be inorganic materials, such as silica gels, or organic compounds such as cross-linked polymers.

"Thermoplastic" describes a material that softens when exposed to heat and which substantially returns to a non-softened condition when cooled to room temperature.

These terms may be defined with additional language in the remaining portions of the specification.

DETAILED DESCRIPTION OF THE PRESENTLY PREFERRED EMBODIMENTS

The present invention is directed to a stretchable, breathable laminate having targeted zones of higher breathability. The material of the present invention is particularly suitable for use as an outer cover for disposable absorbent articles. Examples of such suitable articles include diapers, training pants, incontinence products, swim wear, other personal care or health care garments, or the like.

Referring to FIG. 1, there is shown a cross-sectional view of a breathable laminate 40. The laminate 40 is made up of a breathable, microporous, elastic film 32 and a nonwoven facing material 12 bonded to the film 32. The breathability of the laminate 40, expressed as water vapor transmission rate (WVTR), is essentially equal to the breathability of the film layer 32 when the film 32 and the facing material 12 are initially bonded. The WVTR is a function of both film thickness and film composition. The film layer 32 suitably can deliver moderate breathability, expressed as WVTR, in a range of about 500 to 30,000 grams/m²-24 hours using the Mocon WVTR test procedure described below. Suitably, the moderate WVTR of the film layer 32 is at least about 500 grams/m²-24 hours, even more suitably at least about 750 grams/m²-24 hours, most suitably at least about 1000 grams/m²-24 hours. After the film 32 and the facing material 12 are bonded, the laminate 40 can be stretched in some or all areas of the laminate 40 to impart higher breathability in the stretched zones. A zone of higher breathability is defined as having a WVTR at least 10% higher than an adjacent zone of moderate breathability.

The film 32 is suitably a microporous film which includes an amorphous polymer 42 and filler particles 44. The filler

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particles 44 in the film 32 initiate the formation of voids surrounding the particles upon stretching of the film 32. The voids impart breathability to the film 32 by creating a tortuous path of thin membranes through which water vapor, but not liquid water, can pass. Hence, the laminate 40, including the film 32 and the facing layer 12 bonded together, can be differentially stretched to obtain zones of different breathability. Examples of microporous films are described in U.S. Pat. No. 5,695,868 issued to McCormack, U.S. Pat. No. 5,932,497 issued to Morman, et al., U.S. Pat. No. 6,045,900 issued to Haffner, et al., and U.S. Pat. No. 6,072,005 issued to Kobylivker, et al., all of which are hereby incorporated by reference.

The film polymer 42 may be a low density ethylene elastomer which includes ethylene copolymers having a density less than about 0.90 grams/cm³, desirably from about 0.86 grams/cm³ to about 0.89 grams/cm³ and even more desirably from about 0.87 grams/cm³ to about 0.88 grams/cm³. Suitably, the ethylene elastomers include linear low density polyethylene. The ethylene elastomer suitably includes at least about 50% by weight of the polymeric portion 42 of the film 32, and more suitably from about 70% to 100% by weight. Suitably, the ethylene elastomer includes a polymer wherein the ethylene monomers are polymerized with an alpha-olefin such that the resulting polymer composition has a narrow molecular weight distribution (M_w/M_n) of about 2, homogeneous branching, and controlled long chain branching. Suitable alpha-olefins include, but are not limited to, 1-octene, 1-butene, 1-hexene and 4-methyl-pentene. Exemplary polymers include those made by "metallocene," "constrained geometry" or "single-site" catalysts such as those described in U.S. Pat. No. 5,472,775 to Obijeski, et al. U.S. Pat. No. 5,451,450 to Erdelyi, et al.; U.S. Pat. No. 5,204,429 to Kaminsky, et al.; U.S. Pat. No. 5,539,124 to Eibertson, et al.; and U.S. Pat. No. 5,554,775 to Krishnamurti, et al.; each of which is hereby incorporated by reference.

The metallocene process generally uses a metallocene catalyst which is activated, i.e., ionized, by a co-catalyst. Examples of metallocene catalysts include bis(n-butylcyclopentadienyl)zirconium dichloride, bis(n-butylcyclopentadienyl)zirconium dichloride, bis(cyclopentadienyl)scandium chloride, bis(indenyl)zirconium dichloride, bis(methylcyclopentadienyl)zirconium dichloride, bis(methylcyclopentadienyl)zirconium dichloride, cobaltocene, cyclopentadienyltitanium trichloride, ferrocene, hafnocene dichloride, isopropyl(cyclopentadienyl)-1-fluorenyl zirconium dichloride, molybdocene dichloride, nickelocene, niobocene dichloride, ruthenocene, titanocene dichloride, zirconocene chloride hydride, zirconocene dichloride, among others. A more exhaustive list of such compounds is included in U.S. Pat. No. 5,374,696 to Rosen, et al. and assigned to the Dow Chemical Company. Numerous other metallocene, single-site and/or similar catalyst systems are known in the art.

Regarding metallocene based elastomeric polymers, U.S. Pat. No. 5,204,429 to Kaminsky, et al. describes a process which may produce elastic copolymers from cycloolefins and linear olefins using a catalyst which is a stereorigid chiral metallocene transition metal compound and an aluminoxane. The polymerization is carried out in an inert solvent such as an aliphatic or cycloaliphatic hydrocarbon such as toluene. U.S. Pat. Nos. 5,278,272 and 5,272,236, both to Lai, et al., describe polymers having particular elastic properties, and are both hereby incorporated by reference. Suitable low density ethylene elastomers are commercially available from Dow Chemical Company of Midland, Mich., under the trade name AFFINITY™, includ-

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ing AFFINITY™ EG8200 (5 MI, 0.870 grams/cm³), XU 58200.02 (30 MI, 0.870 grams/cm³), XU 58300.00 (10 MI, 0.870 grams/cm³) and from Exxon Mobil Chemical Co. of Houston, Tex., under the trade name EXACT™ 4049 (4.5 MI, 0.873 grams/cm³); 4011 (2.2 MI, 0.888 grams/cm³); 4041 (3 MI, 0.878 grams/cm³); 4006 (10 MI, 0.88 grams/cm³).

In addition to the amorphous polymer, the polymeric component 42 of the film layer 32 may further include up to about 50% by weight of one or more additional polymers. The film layer 32 may thus also include additional thermoplastic polymers, suitably polyolefins and even more suitably blends and/or copolymers of ethylene and/or propylene. Exemplary polymers include, but are not limited to, polyethylene (homopolymer), linear low density polyethylene (having a density of 0.900-0.935 grams/cm³), ethylene vinyl acetate (EVA), ethylene methyl acrylate (EMA), ethylene normal butyl acrylate (EnBA), flexible polyolefins and/or ethylene-propylene copolymers. In one embodiment, the very low density ethylene elastomer is blended with a second low or medium density polyethylene polymer or copolymer having a density ranging from about 0.90 to about 0.95 grams/cm³. Additional commercially available polyolefin polymer components include, but are not limited to Montell Catalloy Polymer KS350, KS357 and KS359 available from Montell North America, Inc. Montell Catalloy polymer is an olefinic multistep reactor product wherein an amorphous ethylene propylene random copolymer is molecularly dispersed in a predominantly semicrystalline high % propylene monomer/low % ethylene monomer continuous matrix, an example of which is described in U.S. Pat. No. 5,300,365 to Ogle.

The breathable elastic film 32 should not be so thick as to substantially impair its water vapor transmission. For water vapor permeable films the relationship between the WVTR of the films and the thickness of the films may vary due to the affinity of water to the films. Stretched film compositions having somewhat lower water-vapor permeability than the ranges listed should therefore be made into thinner films in order to achieve suitable vapor transmission. For instance, the vapor permeable stretched film composition may be less than about 25.4 micrometers thick, or less than about 12.7 micrometers thick, or less than about 7.62 micrometers thick depending on the strength of the film and the water vapor permeability of the composition.

As mentioned, the filler particles 44 in the film 32 initiate the formation of voids that impart breathability to the film 32 upon stretching. The film 32 may be uniaxially or biaxially stretched. The film 32 is at least minimally stretched to impart breathability to the entire film 32 prior to applying differential, selective stretching. The film 32 may be uniaxially stretched to about 1.1-7.0 times its original length, preferably to about 1.5-6.0 times its original length, most preferably to about 2.5-5.0 times its original length. The film 32 may alternatively be biaxially stretched using conventional techniques familiar to persons skilled in the art.

The film 32 can be initially uniformly stretched to impart a moderate level of breathability across the film 32. In accordance with the invention, the film 32 is further selectively stretched in one or more regions to impart higher breathability to those regions. The selective stretching can be in the same direction as the initial stretching, or can be in a different direction. For instance, the initial stretching and selective further stretching can both be in the machine direction, or one can be in the machine direction and the other in the cross direction.

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Advantageously, the film 32 may be initially stretched using an elevated stretch temperature of about 150–200° F. for most polyolefin-based films. The elevated stretch temperature can be sustained by heating some of the rollers 28, 30. The optimum stretch temperature varies with the type of matrix polymer in the film 32, and is always below the melting temperature of the matrix polymer. The film 32 may also be heated during the subsequent selective stretching, but non-heated selective stretching is preferred.

As used herein, a "filler" is meant to include particulates and/or other forms of materials which can be added to the polymer blend prior to film extrusion, and which will not chemically interfere with or adversely affect the extruded film and, further, which can be uniformly dispersed throughout the film. Generally the fillers 44 will be in particulate form with average particle sizes in the range of about 0.1 to about 7 micrometers, desirably from about 0.1 to about 4 micrometers. As used herein the term "particle size" describes the largest dimension or length of the filler 44. Both organic and inorganic fillers are contemplated for use with the present invention provided they do not interfere with the film forming process and/or subsequent laminating processes. Examples of fillers 44 include calcium carbonate (CaCO_3), various clays, silica (SiO_2), alumina, barium sulfate, talc, magnesium sulfate, titanium dioxide, zeolites, aluminum sulfate, cellulosic powders, diatomaceous earth, gypsum, magnesium carbonate, barium carbonate, kaolin, mica, carbon, magnesium oxide, aluminum hydroxide, pulp powder, wood powder, cellulose derivatives, polymeric particles, chitin and chitin derivatives. The filler particles optionally may be coated with a fatty acid, such as stearic acid or behenic acid, and/or other material in order to facilitate the free flow of the particles (in bulk) and their ease of dispersion into the polymer. The filled film 32 will usually contain at least about 35% filler 44 based upon the total weight of the film layer, more desirably from about 45% to about 65% by weight.

The film 32, prior to stretching, suitably has a basis weight of less than about 100 grams per square meter (g/m^2) and even more suitably less than about 60 g/m^2 . Upon stretching, the film 32 suitably has a basis weight of less than 60 g/m^2 , and even more suitably between about 15 and 35 g/m^2 . Typically, such lower basis weight films have a thickness of about 15 micrometers to about 30 micrometers.

The nonwoven facing material 12 may be a spunbond web and may be formed by known spunbonding processes. The nonwoven material 12 may also be a meltblown web, an air-laid web, a bonded-carded web, or a laminate of two or more nonwoven layers. The nonwoven material 12 may be rendered extensible as explained below. The nonwoven facing material 12 provides a cloth-like feel and appearance on the laminate 40 of the invention.

The facing material 12 can be a nonwoven web necked in the machine direction, thereby imparting cross directional stretch to the material. The process of necking is described in U.S. Pat. No. 5,226,992 issued to Morman, hereby incorporated by reference. The necked material 12 can be bonded at multiple spaced-apart locations to the elastic film 32. After the necked material 12 and the film 32 are bonded, the resulting composite 40 yields cross-directional elasticity.

The term "cross direction," as used herein, refers to the width of a material in a direction generally perpendicular to the direction in which it is produced, as opposed to "machine direction," which refers to the length of a material in the direction in which it is produced. For reference, arrow 49 depicts the machine direction in FIGS. 2 and 3, while the cross direction in FIGS. 2 and 3 is essentially perpendicular

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to the plane of the figures thereby extending into and out of the page. Arrow 48 depicts the cross direction and arrow 49 depicts the machine direction in FIG. 4.

If the nonwoven facing material 12 is necked, fibers of the material 12 should be joined by interfiber bonding to form a coherent web structure which is able to withstand necking. Interfiber bonding may be produced by entanglement between individual meltblown fibers. The fiber entangling is inherent in the meltblown process but may be generated or increased by processes such as, for example, hydraulic entangling or needlepinching. Alternatively and/or additionally a bonding agent may be used to increase the desired bonding. A spunbond web has interfiber bonding caused by thermal bonding of the fibers in the spunbonding process.

The facing material 12 can be elastic in nature, for example, as a spunbond nonwoven produced from a thermoplastic elastomer creating an elastic fiber matrix. Materials suitable for use in preparing an elastic facing material 12 include diblock, triblock, or multi-block elastomeric copolymers such as styrenic copolymers, including styrene-isoprene-styrene, styrene-butadiene-styrene, styrene-ethylene-butylene-styrene, or styrene-ethylene/propylene-styrene, which may be obtained from the Shell Chemical Company, under the trade designation KRATON® elastomeric resin; polyurethanes, including those available from E.I. Du Pont de Nemours Co., under the trade name LYCRA® polyurethane; polyamides, including polyether block amides available from Ato Chemical Company, under the trade name PEBAX® polyether block amide; polyesters, such as those available from E.I. Du Pont de Nemours Co., under the trade name HYTREL® polyester; and single-site or metallocene-catalyzed polyolefins having density less than about 0.89 grams/cm^3 , available from Dow Chemical Co. under the trade name AFFINITY®, also available from Exxon Mobil Chemical Co. under the trade name EXACT™.

A number of block copolymers can be used to prepare the elastic facing material 12 useful in this invention. Such block copolymers generally include an elastomeric midblock portion and a crystalline or amorphous endblock portion. The block copolymers used in this invention generally have a three-dimensional physical crosslinked structure below the endblock portion's glass transition temperature (T_g) and are therefore elastomeric. The block copolymers are also thermoplastic in the sense that they can be melted, formed, and re-solidified several times with little or no change in physical properties (assuming a minimum of oxidative degradation).

Several different methods can be used to synthesize block copolymers. For example, a couple of methods are described on pages 52–53 and 199–200 in the book *Thermoplastic Elastomers, A Comprehensive Review*, edited by N. R. Legge, et al., published by Hanser Publishers, New York. More particularly, one way of synthesizing such block copolymers is to polymerize the crystalline endblock portions separately from the elastomeric midblock portions. Once the midblock and endblock portions have been separately formed, they can be linked. Typically, midblock portions can be obtained by polymerizing di- and tri-unsaturated $\text{C}_6\text{--C}_{10}$ hydrocarbons such as, for example, dienes such as butadiene, isoprene, and the like, and trienes such as 1, 3, 5-heptatriene, and the like. When an endblock portion A is joined to a midblock portion B, an A-B block copolymer unit is formed, which unit can be coupled by various techniques or with various coupling agents C to provide a structure such as A-B-A, which is believed to include two A-B blocks joined together in a tail-to-tail A-B-C-B-A

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arrangement. By a similar technique, a radial block copolymer can be formed having the formula (A-B)_n-C, wherein C is the hub or central polyfunctional coupling agent and n is a number greater than 2. Using the coupling agent technique, the functionality of C determines the number of A-B branches.

Endblock portion A generally includes a poly(vinylarene), such as polystyrene, having an average molecular weight between 1,000 and 60,000. Midblock portion B generally includes a substantially amorphous polyolefin such as polyisoprene, ethylene/propylene polymers, ethylene/butylene polymers, polybutadiene, and the like, or mixtures thereof, having an average molecular weight between about 5,000 and about 450,000. The total molecular weight of the block copolymer is suitably about 10,000 to about 500,000 and more suitably about 200,000 to about 300,000. Any residual unsaturation in the midblock portion of the block copolymer can be hydrogenated selectively so that the content of olefinic double bonds in the block copolymers can be reduced to a residual proportion of less than 5 percent and suitably less than about 2 percent. Such hydrogenation tends to reduce sensitivity to oxidative degradation and may have beneficial effects upon elastic properties.

Suitable block copolymers used in this invention include at least two substantially polystyrene endblock portions and at least one substantially ethylene/butylene midblock portion. As an example, ethylene/butylene typically may include the major amount of the repeating units in such a block copolymer and can constitute, for example, 70 weight-percent or more of the block copolymer. The block copolymer can have three or more arms, and good results can be obtained with, for example, four, five, or six arms. The midblock portion can be hydrogenated, if desired.

Linear block copolymers, such as A-B-A, A-B-A-B-A or the like, are suitably selected on the basis of endblock content, large endblocks being preferred. For polystyrene-ethylene/butylene-polystyrene block copolymers, a styrene content in excess of about 10 weight-percent is suitable, such as between about 12 to about 30 weight-percent. With higher styrene content, the polystyrene endblock portions generally have a relatively high molecular weight. A commercially available example of such a linear block copolymer is a styrene-ethylene/butylene-styrene block copolymer which contains about 13 weight-percent styrene units and essentially the balance being ethylene/butylene units, commercially available from the Shell Chemical Company, under the trade designation KRATON® G1657 elastomer. Typical properties of KRATON® G1657 elastomer are reported to include a tensile strength of 3400 pounds per square inch (2×10⁶ kilograms per square meter), a 300-percent modulus of 350 pounds per square inch (1.4×10⁵ kilograms per square meter), an elongation of 750 percent at break, a Shore A hardness of 65, and a Brookfield viscosity, when at a concentration of 25 weight-percent in a toluene solution, of about 4200 centipoise at room temperature. Another suitable elastomer, KRATON® G2740, is a styrene ethylene/butylene block copolymer blended with tackifier and low density polyethylene.

Other suitable elastomeric polymers may also be used to make the facing material 12. These include, without limitation, elastomeric (single-site or metallocene catalyzed) polypropylene, polyethylene and other alpha-olefin homopolymers and copolymers, having density less than about 0.89 grams/cm³; ethylene vinyl acetate copolymers; and substantially amorphous copolymers and terpolymers of ethylene-propylene, butene-propylene, and ethylene-propylene-butene.

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The elastomeric fibers may be substantially continuous or staple-length, but are preferably substantially continuous. The elastomeric fibers may be produced using a spunbonding process, a meltblowing process, or other suitable processes. The elastomeric fibers may have average diameters of about 1 to 75 micrometers, preferably about 1 to 40 micrometers, more preferably about 1 to 30 micrometers.

The facing material 12 may also be a composite material made of a mixture of two or more different fibers or a mixture of fibers and particulates. Such mixtures may be formed by adding fibers and/or particulates to the gas stream in which meltblown fibers are carried so that an intimately entangled commingling of meltblown fibers and other materials, e.g., wood pulp, staple fibers and particulates such as, for example, hydrocolloid (hydrogel) particulates commonly referred to as superabsorbent materials, occurs prior to collection of the meltblown fibers upon a collecting device to form a coherent web of randomly dispersed meltblown fibers and other materials, such as disclosed in U.S. Pat. No. 4,100,324, the disclosure of which is hereby incorporated by reference.

Referring to FIG. 2, schematically illustrated at 10 is a process for forming a stretchable, breathable laminate 40 with enhanced breathability. A nonwoven facing material 12 is unwound from a supply roll 14 and travels in the direction indicated by the arrow associated therewith as the supply roll 14 rotates in the direction of the arrows associated therewith. The nonwoven facing material 12 passes through a nip 16 of the drive roller arrangement 18 formed by the drive rollers 20 and 22, and then toward a nip 24 of the bonder roller arrangement 26 formed by the bonder rollers 28, 30 where the material 12 meets and is bonded to a breathable, microporous, elastic film 32. Alternatively, the material 12 may be passed, directly in-line with its forming process, through the nip 16 without first being stored on a supply roll.

The breathable, microporous, elastic film 32 is unwound from a supply roll 34 and travels in the direction indicated by the arrow associated therewith as the supply roll 34 rotates in the direction of the arrows associated therewith. The breathable elastic film 32 passes through the nip 24 of the bonder roller arrangement 26 formed by the bonder rollers 28 and 30. The breathable elastic film 32 may also be passed directly through the nip 24 without first being stored on a supply roll. The elastic film 32 may be stretched in one direction (e.g. the machine direction) prior to bonding to the nonwoven material 12, as explained below.

A bonding device 36 applies a bonding material, such as a spray adhesive, onto the facing material 12 at multiple, spaced apart locations, as the material 12 and the film 32 approach the nip 24 of the bonder roller arrangement 26. Thus, once the facing material 12 and the breathable elastic film 32 are nipped together in the bonder roller arrangement 26, a stretchable, breathable laminate 40 is formed.

Breathability in the stretched zones is increased due to the nature of the microporous film 32, which, as mentioned, acquires increased breathability upon stretching. The differential stretching of the laminate 40 may be carried out prior to incorporation of the laminate 40 into a final product, such as an absorbent article. The zones of high breathability are suitably intended for parts of products within close proximity to regions or segments that become saturated with liquid. For example, the crotch region in the outer cover of a diaper is a region that tends to become saturated with liquid. Therefore, having zones of high breathability in the front

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and back areas of the diaper would allow the liquid vapor from the saturated crotch region to escape through the outer cover.

Alternatively, rather than stretching the laminate 40 prior to incorporation into an end product, the laminate 40 can be used in areas of products that will be stretched, thereby letting the laminate-stretching step of the manufacturing process be carried out by the wearer, or a care-giver applying the product to the wearer. For example, an outer cover of a diaper made of the laminate 40 of the invention can have a relatively narrow front and a relatively narrow back, such that the person applying the garment must stretch the front and the back in order to apply the garment to the wearer. As a result of the stretching, the front and the back of the garment achieve greater breathability than the crotch region.

Alternatively, the differential stretching of laminate 40 may be carried out simultaneously with the manufacture of the absorbent article.

In the process 10 shown in FIG. 3, the facing material 12 passes through the nip 16 of the S-roll arrangement 18 in a reverse S-path as indicated by the rotation direction arrows associated with the stack rollers 20 and 22. From the S-roll arrangement 18, the facing material 12 passes through a pressure nip 50 formed by a neck roller arrangement 52. The peripheral linear speed of the rollers of the S-roll arrangement 18 can be controlled to be less than the peripheral linear speed of the rollers of the neck roller arrangement 52, such that the facing material 12 is tensioned between the S-roll arrangement 18 and the pressure nip of the neck roller arrangement 52. By adjusting the difference in the speeds of the rollers, the facing material 12 can be tensioned so that it necks a desired amount. The facing material 12 having mechanically manipulated cross direction stretchability attributable to the necking is then adhesively or thermally joined to the breathable elastic film 32 during their passage through a bonder roller arrangement 26 to form a stretchable, breathable laminate 40. Breathability of the laminate 40, or zones of the laminate 40, can be enhanced by stretching the laminate with a stretching device (not shown).

The facing material 12 component of the laminate 40 is typically open and porous, and does not significantly affect the breathability of the laminate 40. In other words, the moisture breathability of the film 32 should determine the breathability of the laminate 40. However, care should be taken to bond the film 32 and facing material 12 together using techniques that do not significantly disrupt the breathability of the laminate 40. If an adhesive is used, the adhesive should cover only a portion of the total film area, and should be applied as thinly as possible. The preferred adhesive for attaching polyurethane films to a spunbonded web, for example, is a reactive polyurethane-based adhesive available from Shawmut Mills in Bridgewater, Mass. When used, an adhesive should be applied at a basis weight less than about 5.0 grams per square meter (gsm). The adhesive should suitably cover not more than about 75% of the film surface unless the adhesive itself is very water-vapor permeable. Furthermore, any type of bonding that is used, whether it is adhesive, thermal, or any other type, the bonding is suitably discontinuous, thereby bonding the facing material 12 to the film 32 in multiple, spaced-apart locations. The discontinuous bonding does not inhibit or restrict simultaneous movement of the layers the way continuous bonding does, particularly when the film 32 is elastomeric and the facing material 12 is stretchable but does not retract on its own. However, for a given combination of materials, and in view of the herein contained disclosure, the processing conditions necessary to achieve satisfactory bonding can be readily determined by one of skill in the art.

Conventional drive-means and other conventional devices which may be utilized in conjunction with the apparatus of

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FIGS. 2 and 3 are well known and, for purposes of clarity, have not been illustrated in the schematic views of FIGS. 2 and 3.

A perspective view of a stretchable, breathable laminate 40 with selectively enhanced breathability is shown in FIG. 4. Suitably, at least one zone of "higher breathability" is created among the zone or zones of "moderate breathability". The zones of moderate breathability 56 have a WVTR considerably lower than the WVTR of the zones of higher breathability 54. Suitably, the zones of moderate breathability 56 have a WVTR not greater than the WVTR of the film layer 32 before lamination. The zones of higher breathability 54 are zones that have been further stretched by a stretching device (not shown) after the laminate 40 has been formed. These zones of higher breathability 54 suitably have a WVTR at least 10% higher than the WVTR of the zones of moderate breathability 56. More suitably the WVTR of the zones of higher breathability 54 are at least 30% higher than the WVTR of the zones of moderate breathability 56. Most suitably, the WVTR of the zones of higher breathability 54 are at least 50% higher than the WVTR of the zones of moderate breathability 56.

Suitably, the breathable laminate 40 of the invention can stretch between about 50% and 200% in the cross direction, more suitably between about 70% and 170%, most suitably between about 100% and 150%. Similarly, when a facing material 12 having machine direction stretchability is used to make the laminate 40, the stretchability of the laminate 40 in the machine direction is suitably between about 50% and 200% in the machine direction, more suitably between about 70% and 170%, most suitably between about 100% and 150%. The laminate 40 suitably recovers at least 40% of its elongation upon retraction in the cross direction and at least in the machine direction if an elastomeric facing material 12 is used, more suitably at least 50% of its elongation is recovered, and desirably not more than 75% of the elongation is recovered. If the elongation totally recovers, the breathability may be impeded by closing of the micropores. Elastic tension capabilities of the laminates are generally determined by the type and basis weight of the film components, however, the facing type and lamination method can impact tension properties, permanent set and hysteresis properties of the resulting laminate 40. As a result, machine direction and cross direction properties can be altered by the type of facing and lamination technique used.

For example, with reference to FIGS. 5, 6 and 7, if it is desired to prepare a composite breathable laminate that is stretchable to at least 150% elongation, a width of neckable material shown schematically and not necessarily to scale in FIG. 5 having a width "A" such as, for example, 250 cm, is tensioned so that it necks down to a width "B" of about 100 cm. The necked material shown in FIG. 6 is then joined to an elastic sheet (not shown) having a width of approximately 100 cm and which is at least stretchable to a width of 250 cm. The resulting composite elastic necked-bonded material shown schematically and not necessarily to scale in FIG. 7 has a width "B" of about 100 cm and is stretchable to at least the original 250 cm width "A" of the neckable material for an elongation of about 150%. As can be seen from the example, the elastic limit of the elastic sheet needs only to be as great as the minimum desired elastic limit of the composite elastic necked-bonded material.

For the following examples, four different combinations of breathable, microporous films and nonwoven facing materials were laminated and stretched in laminate form, resulting in laminates in accordance with the present invention. The composition of the laminates is shown in Table 1.

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TABLE 1

Composition of Cycled Laminates

Sample	Film	Resin	Stabilizer	CaCO ₃	Film Basis Weight (grams/m ²)	Spunbond Necking Level
1	XSF-638	8200*/1845**	E 17	55% Omya	60	45%
2	XSF-638	8200*/1845**	E 17	55% Omya	100	35%
3	XSF-638	8200*/1845**	E 17	55% Omya	100	60%
4	XSF-638	8200*/1845**	E 17	55% Omya	100	45%

*8200 is AFFINITY @ EG8200, 0.870 g/cc

**1845 is AFFINITY @ PL 1845, 0.910 g/cc

Each of the film layers was adhesively bonded to the corresponding facing material using REXTAC™ 2730 adhesive from Huntsman. Once the laminates were formed, each laminate was cycled. The breathability of each laminate, both prior to and after cycling, is shown in Table 2.

Cycling was carried out using a constant-rate-of-extension tensile tester, designated as Sintech 2, Model 3397-139, available from Sintech Corporation, Cary, N.C. Each laminate test sample was approximately 4.5 inches by 3 inches, with the 4.5 inch side being in the cross direction. Each 3-inch wide specimen was clamped by two pneumatic jaws so that the gauge length (jaw separation) was 2 inches, and the direction of pull was in the cross direction. The pulling speed was set at 500 mm/min. Testing was done throughout four extension/retraction cycles, during which the specimen was first pulled to 100% elongation (4-inch jaw separation), the jaws then stopped and immediately returned to the starting gauge length, then three more extension-retraction cycles were repeated. Breathability of each sample was measured, both before and after cycling, using the Mocon WVTR test procedure described below.

TABLE 2

Breathability of Cycled Laminates

Sample	Initial WVTR (grams/m ² · 24 hours)	Post-Cycling WVTR (grams/m ² · 24 hours)
1	7377	3055
2	1855	2880
3	1180	2730
4	603	2587

It will be appreciated that details of the foregoing embodiments, given for purposes of illustration, are not to be construed as limiting the scope of this invention. Although only a few exemplary embodiments of this invention have been described in detail above, those skilled in the art will readily appreciate that many modifications are possible in the exemplary embodiments without materially departing from the novel teachings and advantages of this invention. Accordingly, all such modifications are intended to be included within the scope of this invention, which is defined in the following claims and all equivalents thereto. Further, it is recognized that many embodiments may be conceived that do not achieve all of the advantages of some embodiments, particularly of the preferred embodiments, yet the absence of a particular advantage shall not be construed to necessarily mean that such an embodiment is outside the scope of the present invention.

Test Procedure for Water Vapor Transmission Rate (WVTR)

A suitable technique for determining the WVTR (water vapor transmission rate) value of a film or laminate material of the invention is the test procedure standardized by INDA (Association of the Nonwoven Fabrics Industry), number IST-70.4-99, entitled "STANDARD TEST METHOD FOR WATER VAPOR TRANSMISSION RATE THROUGH NONWOVEN AND PLASTIC FILM USING A GUARD FILM AND VAPOR PRESSURE SENSOR" which is incorporated by reference herein. The INDA procedure provides for the determination of WVTR, the permeance of the film to water vapor and, for homogeneous materials, water vapor permeability coefficient.

The INDA test method is well known and will not be set forth in detail herein. However, the test procedure is summarized as follows. A dry chamber is separated from a wet chamber of known temperature and humidity by a permanent guard film and the sample material to be tested. The purpose of the guard film is to define a definite air gap and to quiet or still the air in the air gap while the air gap is characterized. The dry chamber, guard film, and the wet chamber make up a diffusion cell in which the test film is sealed. The sample holder is known as the Permatran-W Model 100K manufactured by Mocon/Modern Controls, Inc., Minneapolis, Minn. A first test is made of the WVTR of the guard film and the air gap between an evaporator assembly that generates 100% relative humidity. Water vapor diffuses through the air gap and the guard film and then mixes with a dry gas flow which is proportional to water vapor concentration. A sensor generates a signal proportional to the vapor content of the gas stream. The electrical signal is routed to a computer for processing. The computer calculates the transmission rate of the air gap and the guard film and stores the value for further use.

The transmission rate of the guard film and air gap is stored in the computer as CalC. The sample material is then sealed in the test cell. Again, water vapor diffuses through the air gap to the guard film and the test material and then mixes with a dry gas flow that sweeps the test material. Also, again, this mixture is carried to the vapor sensor. The computer then calculates the transmission rate of the combination of the air gap, the guard film, and the test material. This information is then used to calculate the transmission rate at which moisture is transmitted through the test material according to the equation:

$$TR_{\text{test material}} = \frac{TR_{\text{test material, guardfilm, airgap}}}{\text{guardfilm, airgap}} \cdot TR^{-1}$$

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Calculations:

WVTR: The calculation of the WVTR uses the formula:

$$WVTR = F_{psat}(T)RH(Ap_{sat}(T)(1 - RH))$$

where:

F=The flow of water vapor in cc/min.,

$P_{psat}(T)$ =The density of water in saturated air at temperature T,

RH=The relative humidity at specified locations in the cell,

A=The cross sectional area of the cell, and,

$P_{psat}(T)$ =The saturation vapor pressure of water vapor at temperature T.

We claim:

1. A breathable laminate, comprising:

a breathable, microporous, elastic film; and
a nonwoven facing material bonded to the film;

wherein the laminate is selectively stretched to form at least one stretched zone thereof resulting in zones of differential breathability comprising at least one zone of higher breathability and at least one zone of moderate breathability;

wherein the at least one stretched zone of the laminate consists of the at least one zone of higher breathability; and

wherein each of the zones of differential breathability comprises a portion of the film and a portion of the nonwoven facing material.

2. The laminate of claim 1, wherein the at least one zone of higher breathability has a water vapor transmission rate at least 10% higher than a water vapor transmission rate of the at least one zone of moderate breathability.

3. The laminate of claim 1, wherein the at least one zone of higher breathability has a water vapor transmission rate at least 30% higher than a water vapor transmission rate of the at least one zone of moderate breathability.

4. The laminate of claim 1, wherein the at least one zone of higher breathability has a water vapor transmission rate of at least 50% higher than a water vapor transmission rate of the at least one zone of moderate breathability.

5. The laminate of claim 1, wherein the water vapor transmission rate of the at least one zone of moderate breathability is at least about 500 grams/m²-24 hours.

6. The laminate of claim 1, wherein the water vapor transmission rate of the at least one zone of moderate breathability is at least about 750 grams/m²-24 hours.

7. The laminate of claim 1, wherein the water vapor transmission rate of the at least one zone of moderate breathability is at least about 1000 grams/m²-24 hours.

8. The laminate of claim 1, wherein the laminate is elastomeric.

9. The laminate of claim 1, wherein the facing material is necked.

10. The laminate of claim 1, wherein the facing material is elastomeric.

11. The laminate of claim 1, wherein the at least one selectively stretched zone is stretched at least twice.

12. The laminate of claim 1, wherein the laminate can be stretched by about 50% to about 200% in a cross direction.

13. The laminate of claim 1, wherein the laminate can be stretched by about 70% to about 170% in a cross direction.

14. The laminate of claim 1, wherein the laminate can be stretched by about 100% to about 150% in a cross direction.

15. The laminate of claim 1, wherein the laminate can be stretched by about 50% to about 200% in a machine direction.

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16. The laminate of claim 1, wherein the laminate can be stretched by about 70% to about 170% in a machine direction.

17. The laminate of claim 1, wherein the laminate can be stretched by about 100% to about 150% in a cross direction.

18. An absorbent article outer cover comprising the laminate of claim 1.

19. An outer cover for absorbent articles, comprising a breathable laminate;

the breathable laminate including a breathable, microporous, elastic film and a nonwoven facing material bonded to the film;

wherein the laminate is selectively stretched to form at least one stretched zone thereof resulting in zones of differential breathability comprising at least one zone of higher breathability and at least one zone of moderate breathability;

wherein the at least one stretched zone of the laminate consists of the at least one zone of higher breathability; and

wherein each of the zones of differential breathability comprises a portion of the film and a portion of the nonwoven facing material.

20. The outer cover of claim 19, wherein the laminate is selectively stretched to form at least one stretched zone prior to incorporation in the absorbent article.

21. The outer cover of claim 19, wherein the laminate is selectively stretched to form at least one stretched zone subsequent to incorporation in the absorbent article.

22. The outer cover of claim 19, wherein the laminate is selectively stretched to form at least one stretched zone as the absorbent article is applied to a wearer.

23. The outer cover of claim 19, wherein the laminate has a water vapor transmission rate of at least about 500 grams/m²-24 hours in the zone of moderate breathability.

24. The outer cover of claim 19, wherein the laminate has a water vapor transmission rate of at least about 750 grams/m²-24 hours in the zone of moderate breathability.

25. The outer cover of claim 19, wherein the laminate has a water vapor transmission rate of at least about 1000 grams/m²-24 hours in the zone of moderate breathability.

26. The outer cover of claim 19, wherein the facing material is necked.

27. The outer cover of claim 19, wherein the facing material is elastomeric.

28. The outer cover of claim 19, wherein the at least one selectively stretched zone is stretched at least twice.

29. A method of making an outer cover for absorbent articles, comprising the steps of:

forming a breathable laminate by bonding a nonwoven facing material to a breathable, microporous, elastic film; and

selectively stretching the breathable laminate to form at least one stretched zone thereof resulting in zones of differential breathability comprising at least one zone of higher breathability and at least one zone of moderate breathability;

wherein the at least one stretched zone of the laminate consists of the at least one zone of higher breathability; and

wherein each of the zones of differential breathability comprises a portion of the film and a portion of the nonwoven facing material.

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30. The method of claim 29, further comprising the step of selectively stretching the laminate to format at least one stretched zone prior to incorporation of the laminate in the absorbent article.

31. The method of claim 29, further comprising the step 5 of selectively stretching the laminate to form at least one stretched zone subsequent to incorporation of the laminate in the absorbent article.

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32. The method of claim 29, further comprising the step of selectively stretching the laminate to form at least one stretched zone as the absorbent article is applied to a wearer.

* * * * *

Appendix C – Related Proceedings Appendix

None